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AN INVESTIGATION INTO THE COMPOSITION OF AMMONIACAL LIQUOR

III—IMPROVEMENTS IN ROUTINE ANALYSIS

By L. Barker, B.Sc., Ph.D., A.R.I.C., and N. W. Hollingworth, B.Sc.
University of Leeds

Research Communication GC70

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I SUMMARY

Results obtained from the chromatographic analysis of the phenols in a number of ammoniacal liquors have been employed in an attempt to improve the accuracy of existing analytical procedures.

Determination of total monohydric phenols requires them first to be separated from dihydric phenols by steam distillation, and a detailed investigation has been made, under various conditions, of the steam volatilities of many phenols known to be present in liquors. It is shown that some dihydric phenols (catechols) are appreciably volatile during the distillation of their aqueous solutions and that oxidation products formed from these compounds are also steam-volatile, though steam distillation of both catechols and their oxidation products is prevented by the presence of lead salts. It was found that some monohydric phenols can be distilled from strongly alkaline solutions. Steam volatilities of organic bases are considered, and a table is included that gives results of the identification and determination of a number of these compounds in two ammoniacal liquors.

In the determination of total monohydric phenols by bromination, the presence of an excess of bromine results in most phenols taking up a greater amount of bromine than would be theoretically expected. Factors can be calculated to relate the absorption of bromine to the total concentration of monohydric phenols in a liquor, and these factors appear to be substantially constant for liquors produced by the same process. If the excess bromination method has been used in the past and total monohydric phenols calculated in terms of phenol, then results will have been nearly 10 per cent below the correct figure.

A study of the permanganate values of compounds present in ammoniacal liquors has been made. Some values are significantly different from those at present accepted, and it has not always been possible to discover where the discrepancy occurred. From the experimentally determined total permanganate value of a liquor and the sum of the permanganate values of its known constituents, the "difference figure" that can result from the presence of unidentified compounds has been assessed. The average difference figure for all types of liquors is about 600 p.p.m. This value appears to be significant for coke oven liquors, but for other liquors the accumulated errors could attain such a proportion, some difference figures having been negative quantities and one being zero.

At present, the only satisfactory rapid method for the determination of total phenols and total dihydric phenols in a liquor is by ultraviolet spectrophotometry. Errors arising in the procedure given in a previous Paper have been reduced, and factors have been calculated for use with all types of liquors.

II INTRODUCTION

During the last decade, the Joint Research Committee of The Gas Council and the University of Leeds has been engaged upon problems of Gas Works' effluent disposal. Part of this investigation has involved the identification and quantitative determination of the organic constituents (mainly the phenols) present in ammoniacal liquors. A description has already been given of the techniques employed and of the results obtained in the analysis of a number of liquors representative of the British Gas and Coking Industries; these were included in three Research Communications presented to The Institution of Gas Engineers.[1, 2, 3]

It was considered that the detailed information that had been assembled might be used to yield more realistic results from analytical procedures employed in routine analysis. Thus, in the determination of monohydric phenols by bromination, the factor that is used to convert the amount of bromine absorbed into a figure for the concentration of phenols gives the final result in terms of phenol and takes no account of the mixture of different phenols that is present in the liquor. Since the concentration in the liquor of each monohydric phenol is now known from the chromatographic analysis, and the amount of bromine that each phenol absorbs per unit weight can be determined, then a correct bromination factor can be obtained. For practical use, the factor must cover a wide range of liquors, and should especially not vary with liquors produced by a given process. The present investigation has thus involved the determination of the bromine equivalents of a number of phenols, and these have been coupled with the results of the chromatographic analyses for calculation of the factors.

In a similar manner, new factors have been obtained for the permanganate values, and here it has also been possible to re-assess the "difference figure" that is always obtained in liquor analysis; previously, no account could be taken of the dihydric phenols.

The omission of precise instructions in a part of the procedure for the separation of monohydric phenols from dihydric phenols has required a study of the steam volatilities of the phenols, and has led to some interesting observations concerning their distillation under different conditions. Experimental results are given in more detail than required for present purposes, but such information does not appear to have been recorded previously and should be of use to those engaged in the analysis of phenols.

III SEPARATION OF LIQUOR CONSTITUENTS BY STEAM DISTILLATION

(A) INTRODUCTION

In the analysis of ammoniacal liquors, steam distillation is employed for the separation of monohydric phenols from constituents that would interfere with their determination. The term "steam distillation" used in liquor analysis should first be explained. It is not the practice to employ the traditional apparatus of organic chemistry, involving the passage of steam through the solution from which the solute is to be recovered, but simply to distil the aqueous solution with or without the addition of water to the distilling flask during the operation. The procedure most often used in Gas Works' laboratories to determine the phenolic content of liquors is that given in Key's "Gas Works Effluents and Ammonia".[4] This involves bromination; and, to assist in the subsequent discussion, the relevant part of the preliminary treatment is indicated here, being taken from the second (revised and enlarged) edition of the manual (pp. 160 and 161).

Crude liquors may first require the removal of cyanide and sulphide, the procedure being omitted with spent liquors. Then, 50 ml of the sample is evaporated on a water bath with 25 ml of 50 per cent sodium hydroxide solution until salts begin to separate. This residue is washed into a distilling flask and made slightly acid with 30 per cent sulphuric acid. After the addition of a pinch of lead carbonate, the solution is neutralized with 2g of calcium carbonate; 25 to 30 g of sodium chloride is added, and 250 ml of solution distilled off, the liquid level in the flask being kept constant during the distillation by the addition of water from a dropping funnel. Monohydric phenols in the distillate are then determined by bromination.

The reasons for the different steps are not given in the manual. The evaporation of the solution in presence of sodium hydroxide serves to remove organic bases, which are volatile in steam; lead carbonate is added prior to the distillation of monohydric phenols, to retain any sulphide that might be present in spent liquors; calcium carbonate is used to retain thiocyanic acid; and salt is presumably employed to increase the rate of phenol distillation.

When this procedure was followed, it was suspected that low estimates were being obtained for the amounts of monohydric phenols in ammoniacal liquors. This was confirmed when phenol was determined in a solution of known concentration, results being substantially below the correct value. The discrepancy between the observations was found to result from the fact that, if a constant volume of liquid was maintained in the distilling flask, it was necessary to distil off much more than 250 ml of solution to remove all the phenol from it.

(B) Previous Investigations

The literature was therefore examined, firstly to find existing information on the steam distillation of phenols, secondly to trace the present method to its origins, and thirdly to discover if the method was different from those used by other authorities concerned with phenol determinations.

(i) *Steam Volatilities of Phenols*

Apart from phenol, there appears to be very little quantitative data on the distillation of other phenols in presence of steam. Key and Etheridge[5] distilled a solution of phenol in water (concentration about 5 g/l.) and determined how the amount of phenol that distilled over was dependent on the amount of distillate collected; their results are given in Table 1. Also included in Table 1 are results by Dannis[6], who distilled phenol from aqueous solution (concentration range 5 to 400 p.p.m.) adjusted to pH4 with phosphoric acid. The ratio (n) of the concentration of phenol in the vapour phase to that in the aqueous phase can be determined from these results. Key's calculations of n are given in Table 1; values calculated from the results of Dannis are also included. The average value of n given by Key is 1·83, that of Dannis being about 2·1. The difference may be due to the pH of the solutions in the distilling flask. Key and Etheridge also made determinations with *p*-cresol and *m*-cresol, but they give only calculated n values, which are shown here in Table 2.

TABLE 1.—*Distillation of Aqueous Phenol Solutions.*

Key and Etheridge[5]			Dannis[6]		
Solution Distilled (per cent)	Phenol Distilled (per cent)	n	Solution Distilled (per cent)	Phenol Distilled (per cent)	n
1	2	3	4	5	6
2	3·6	1·82	9	18	2·10
5	8·9	1·82	18	34	2·09
10	17·3	1·84	27	49	2·14
20	33·3	1·81	36	62	2·17
30	47·9	1·83	46	72	2·07
40	60·8	1·83	55	81	2·08
50	72·0	1·84	64	88	2·08
60	81·5	1·84	73	93	2·03
75	92·2	1·79	82	96	1·88
			91	98	1·62

TABLE 2.—*Ratio of Phenol Concentrations in Vapour and Aqueous Phases.* (n).

Compound	n
1	2
Phenol	1·83
p-Cresol	2·75
m-Cresol	2·41

These figures indicate that the cresols are more volatile in steam than is phenol. The authors state that catechol is definitely non-volatile in steam. One further point is given in a paper by Ettinger and Ruchhoft[7] and refers to unpublished memoranda of S. Megregian, which indicate that there can be a progressive loss of phenol in concentrating an alkaline solution.

(ii) *Origin of the Method Given by Key*

It will be clear from this quantitative information that practically all the solution must be distilled over in order to recover all the phenol. Examination of the method cited in the second edition of Key's manual gives no indication of the volume of liquid originally in the distilling flask, and hence the proportion of the solution that has been distilled over cannot be determined. Obviously, the original volume should not be much greater than 250 ml if the liquid in the flask is not replenished, though the constant addition of water to the distilling flask will adversely affect the amount of phenol that distils over. On the other hand, the presence of salt will increase the rate of phenol distillation; but information is not available to determine the extent of the two opposing effects.

Referring back to the first edition of Key's manual, the preliminary treatment is almost identical with that given in the second edition, except there is no indication that the volume of liquid in the distilling flask is to be kept constant throughout the distillation. Again the volume of liquid in the distilling flask at the start is not given.

The analytical methods quoted in the manual have been taken from two publications of the Alkali Inspectors.[8, 9] The later of these two publications[9] gives an identical preliminary treatment of the sample to that in the second edition of Key's manual, where the liquid in the distilling flask is maintained at a constant level; this procedure is ascribed to Skirrow—Titherley. The previous publication[8], quotes the Skirrow[10] method which is a more detailed though tedious procedure for the distillation of the phenols, but would undoubtedly lead to a better recovery. Here, the alkaline residue, after removal of the bases, is diluted to about 150 ml with water and then acidified. This is distilled until salts crystallize out and the procedure twice repeated with addition of 100 ml of water to the residue each time. These distillates are subsequently freed from thiocyanic acid and hydrogen sulphide by treatment with calcium carbonate and lead carbonate, then redistilled. It is apparent that the extent to which the solution must be distilled to remove all the phenol is clearly recognized in this earlier method. Thus, although the attempt has since

been made to simplify the procedure, it has led to error by ignoring the steam distillation behaviour of phenol.

(iii) *Methods Given by Other Authorities*

Other investigators have recognized that it is necessary to distil the bulk of the solution to remove all the phenol, many of the procedures being concerned with sewage and water analysis where phenols are usually present in concentrations far smaller than in ammoniacal liquors, and separations from dihydric phenols are normally ignored. Theriault[11], and Beshgetoor[12], suggest that 90 per cent of the solution should be distilled to remove the phenols. In the "Standard Methods for the Examination of Water, Sewage and Industrial Wastes"[13], the phenol is distilled from a solution made acid to less than pH4 with phosphoric acid, 450 ml of distillate being collected from 500 ml of solution. Then 50 ml of water is added to the distilling flask and distillation continued until a total of 500 ml has been collected.

A publication of the Ministry of Housing and Local Government[14] suggests that the monohydric phenols should be distilled at pH8, and that 100 ml of distillate should be collected from 110 ml of solution in the distilling flask. A second procedure given in this book is similar to that in Key's manual, except that, after acidification of the residue from the alkaline evaporation and the addition of calcium carbonate and sodium chloride, 250 ml of water is added, and 250 ml of distillate is subsequently collected.

The A.B.C.M.—S.A.C. Joint Committee[15] suggests a similar method. For the removal of amines, only 20 per cent of the solution is distilled off instead of reducing the volume until salts separate. Here the volume of the residue left after the distillation of monohydric phenols from acid solution will be small, since the volume distilled is to be equal to that of the original sample, and, as a result of distilling the bases, the only increase in volume of the sample that has occurred is in washing the precipitate of lead sulphide (during sulphide removal) with a small volume of water. Indeed, it is suggested that a small volume of water may be added to the contents of the distilling flask to enable collection of the required volume of distillate.

(c) Steam Distillation of Phenols

This review of the literature indicated the data that it would be useful to determine for use in the analysis of ammoniacal liquors. Thus:

(1) The steam volatilities of all monohydric phenols known to be present in ammoniacal liquor.

(2) The influence of maintaining a constant liquid level in the distilling flask and the presence of acid and salts on the steam volatilities of phenols.

(3) The extent to which dihydric phenols might be volatile in steam, since these compounds should not be distilled with the monohydric phenols.

(4) The extent to which monohydric phenols might be distilled from alkaline solutions in the procedure for removal of bases.

(i) *Apparatus and Procedure*

For most of the investigation, the apparatus used was a Kjeldahl distillation assembly (Quickfit and Quartz No. 280A) comprising a one-litre flask with splash head and vertical condenser. Solutions of phenols in water were prepared at concentrations of approximately 1 g/1; and 25 ml of the solution was pipetted into the distilling flask. To this was added 475 ml of water, resulting in a phenol concentration of about 50 p.p.m. Nine 50-ml fractions of the distillate were collected in Crow receivers, leaving a residue of 50 ml in the flask. The proportion of the phenol in each fraction was determined by ultraviolet spectrophotometry, measuring the optical density at the wavelength of maximum absorption for the particular compound. It was not necessary to convert the determination to concentration, since only the percentage of the phenol that had distilled was required, this could be calculated from the optical density of the original phenol solution.

(ii) *Distillation from Neutral Solution*

The result of distilling a number of monohydric and dihydric phenols from approximately neutral solution is given in Table 3. All these phenols are known to be present in ammoniacal liquors, though the concentrations of

Table 3.—*Distillation of Phenols from Neutral Solution.*

Compound	Solution Distilled (per cent)										n
	10	20	30	40	50	60	70	80	90	In Residue	
	Phenol Distilled (per cent)										
1	2										3
Phenol	19·4	36·5	51·4	64·2	74·8	83·8	90·7	95·6	98·5	1·5	2·0
o–Cresol	41·6	66·7	82·2	91·4	96·2	98·5	99·6				5·0
m–Cresol	25·3	45·4	61·7	74·8	84·6	91·6	96·1	98·7	99·8		2·7
p–Cresol	25·7	46·4	63·0	76·1	85·7	92·3	96·6	98·9	99·8		2·8
2,6–Xylenol	78·8	95·1	98·7	99·5							14·1
2,5–Xylenol	52·1	78·5	91·3	96·9	99·2	99·8					6·9
2,4–Xylenol	53·3	79·2	91·5	97·1	99·3						7·0
2,3–Xylenol	42·3	68·1	83·5	91·9	96·3	98·5	99·6				5·1
3,5–Xylenol	34·2	57·9	74·7	86·0	93·0	97·0	99·0	99·9	100·0		3·9
3,4–Xylenol	24·8	46·2	62·5	75·5	85·1	91·9	96·3	98·8	99·8		2·75
2–Ethylphenol	59·8	84·2	94·5	98·5	100·0						8·3
3–Ethylphenol	35·0	58·8	75·6	86·2	92·8	96·6	98·7	99·7			4·0
4–Ethylphenol	35·4	59·9	76·4	87·2	93·8	97·5	99·2				4·1
3–Methyl–5–ethylphenol	44·5	70·6	85·3	93·3	97·3	99·2					5·5
4–Indanol	21·6	39·3	54·9	68·1	78·7	87·3	93·5	97·9	100·3		2·25
5–Indanol	15·7	30·2	43·6	55·7	66·8	76·7	85·2	92·0	97·2	2·8	1·60
1–Naphthol	5·0	10·5	16·2	22·4	29·2	36·8	45·4	55·8	69·5	30·5	0·50
2–Naphthol	2·7	5·7	9·0	12·7	16·8	21·6	27·4	34·8	45·6	54·4	0·27
Catechol	0·2	0·4	0·5	0·7	0·9	1·1	1·4	1·9	2·9	97·1	0·014
3–Methylcatechol	0·6	1·3	2·0	2·9	4·0	5·2	6·9	9·2	13·2	86·8	0·059
4–Methylcatechol	0·2	0·5	0·8	1·1	1·4	1·8	2·3	3·1	4·8	95·2	0·020
Resorcinol	0·1	0·1	0·1	0·2	0·4	0·6	0·8	1·1	1·7	98·3	0·007
2–Methylresorcinol	0·1	0·1	0·2	0·2	0·2	0·2	0·3	0·6	1·4	98·6	0·004
5–Methylresorcinol						0·0	0·1	0·3	0·5	99·5	0·002
Quinol	0·2	0·4	0·6	0·8	0·9	1·0	1·1	1·4	2·2	97·8	0·014

ethylmethylphenols, indanols and naphthols are usually trivial. There is also included in Table 3 the ratio (n) of the concentration of the phenol in the vapour phase to that in the aqueous phase, which can be calculated from the equation:

$$\log_{10}(100 - x) = \frac{1}{n}\log_{10}(1 - \frac{y}{100}) + 2$$

where x is the percentage of water that has distilled from the flask and y the percentage of phenol that has then distilled with it. The value of n was calculated for each distillate fraction, that in Table 3 being an average of these values, there being sometimes a tendency for the value of n either to rise or fall during the distillation. Comparison with results of Key in Table 2 indicates a similarity between the n values for *p*-cresol, but the values for phenol and *m*-cresol are greater in Table 3. The n value for phenol calculated from the results of Dannis and given in Table 1 agrees better with the value quoted here.

It will be seen that, apart from the naphthols, phenol is the least volatile of the monohydric phenols, and, as indicated earlier, it is necessary to distil over practically all of the solution for quantitative recovery. All other monohydric phenols that are important in ammoniacal liquors would be quantitatively recovered by distillation of 90 per cent of the solution. It is interesting that substitution by alkyl groups in the *meta* and *para* positions to the hydroxyl group give compounds that are only a little more volatile than phenol, the *para* substituent having a greater effect than the *meta*. The presence of an alkyl group in the *ortho* position markedly increases the steam volatility; this is particularly noticeable with 2,6-xylenol, which contains two methyl groups in positions *ortho* to the hydroxyl and is about seven times more volatile than phenol. This is an example of the "*ortho*-effect", where substituents in *ortho* positions tend to depress the character of the hydroxyl group.

As the alkyl group increases in size, the corresponding phenols increase in steam volatility, though the ring containing three saturated carbon atoms in the indanols apparently has so little influence that their volatilities are comparable with that of phenol. The presence of two fused rings in the naphthols results in them being relatively less volatile than any of the other monohydric phenols, and it would be impracticable to recover them quantitatively by steam distillation.

It has been indicated previously that dihydric phenols are not volatile in steam, and Table 3 shows that resorcinols and quinol are only very slightly volatile. The catechols, especially 3-methylcatechol, are more volatile in steam than had been expected. Hence, if steam distillation is used in an attempt to separate monohydric from dihydric phenols, a proportion of the catechols will be found in the distillate. This assumes that the separation is carried out from neutral solution, but it will be seen later that the volatility of the catechols in steam may be suppressed by the presence of lead salts. Although no experimental evidence can be cited, it may be expected that dimethyl- and ethyl-catechols will be even more steam-volatile than the methylcatechols.

An important factor arising from these observations is that, in procedures whereby dilute aqueous solutions of dihydric phenols are evaporated to attain a concentration suitable for subsequent analysis, an appreciable loss of catechols would result.

(iii) *Distillation from Acid Solution*

Table 4 contains the results of a series of distillations from acid solution, where the 500 ml of phenol solution contained 5 ml of concentrated hydrochloric acid. Only the monohydric phenols are included in Table 4. Comparison with Table 3 indicates that the addition of acid has only a small influence on the steam volatility of a phenol. In most instances, there is a slight increase in volatility, though sometimes the differences are hardly significant.

(iv) *Distillation from Salt Solution*

To the 500 ml of phenol solution was added 30 g of sodium chloride, and the resulting solution was distilled. The results are given in Table 5, and it will be seen that in each case there is a substantial increase in the rate of distillation of the phenol. Under these conditions, all the important phenols in ammoniacal liquor would be recovered quantitatively if 80 per cent of the solution were distilled, and almost complete recovery of the naphthols is possible from this medium. The addition of salt, adversely affects separations of monohydric from dihydric phenols, the methylcatechols being particularly volatile from such a solution.

TABLE 4.—*Distillation of Phenols from Acid Solution.*

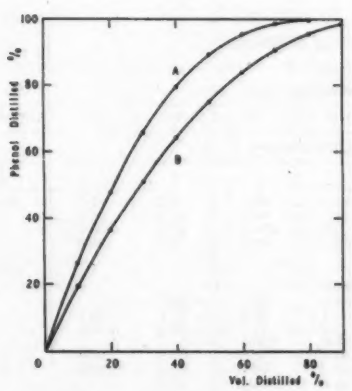
Compound	Solution Distilled (per cent)										n
	10	20	30	40	50	60	70	80	90	In Residue	
	Phenol Distilled (per cent)										
1	2										3
Phenol	19·8	37·3	51·0	65·7	76·7	85·7	92·4	97·2	99·7		2·1
o-Cresol	44·6	70·6	85·6	93·5	97·5	99·1	99·7	99·8	99·8		5·5
m-Cresol	26·1	47·1	63·6	76·5	86·2	92·8	96·9	99·1	100·0		2·85
p-Cresol	26·4	47·8	64·6	77·5	86·8	93·1	97·1	99·2	99·8		2·9
2,6-Xylenol	80·2	96·0	99·4	100·3							14·9
2,5-Xylenol	56·3	81·9	93·7	98·7	100·5						7·7
2,4-Xylenol	53·7	79·9	92·0	97·3	99·3	100·0					7·2
2,3-Xylenol	42·6	68·5	83·8	92·4	96·9	98·6	99·3	99·8			5·2
3,5-Xylenol	34·1	58·1	75·0	85·9	93·0	97·1	99·0	99·9	100·0		3·9
3,4-Xylenol	26·4	47·4	64·0	76·8	86·3	92·8	97·1	99·5	100·4		2·9
2-Ethylphenol	60·3	85·0	94·5	98·1	99·4	99·9	100·1				8·5
3-Ethylphenol	35·0	59·2	75·7	86·4	92·8	96·4	98·0	98·7	98·9		4·0
4-Ethylphenol	36·1	60·7	77·3	87·8	94·1	97·5	99·1	99·6	99·8		4·2
3-Methyl-5-ethylphenol	45·3	71·4	86·2	93·8	97·5	99·0	99·4	99·6			5·6
4-Indanol	22·2	41·3	57·3	70·4	81·2	89·6	95·8	99·6	101·7		2·4
5-Indanol	16·2	31·2	44·9	57·3	68·5	78·3	86·7	93·2	97·8	2·2	1·67
1-Naphthol	5·3	11·0	17·0	23·6	30·8	38·7	47·7	58·3	72·4	27·6	0·52
2-Naphthol	2·7	5·6	8·8	12·3	16·2	20·8	26·1	33·3	44·2	55·8	0·26

TABLE 5.—*Distillation of Phenols from Salt Solution.*

Compound	Solution Distilled (per cent)										n
	10	20	30	40	50	60	70	80	90	In Residue	
	Phenol Distilled (per cent)										
1	2										3
Phenol	26·4	47·9	65·8	79·5	89·3	95·5	98·7	99·7	99·7		3·0
o–Cresol	59·8	85·5	95·8	99·4	100·2						8·6
m–Cresol	36·5	61·8	79·5	90·3	96·3	99·0	99·9	99·9			4·3
p–Cresol	36·9	62·5	80·1	91·0	96·8	99·2	99·9	100·0			4·4
2,6–Xylenol	91·7	99·8	100·8								24
2,5–Xylenol	71·9	93·3	99·0	100·3							12
2,4–Xylenol	71·1	92·3	98·3	99·6	99·8						12
2,3–Xylenol	60·9	86·4	96·6	99·7	100·6						9·0
3,5–Xylenol	50·3	77·2	91·3	97·4	99·7	100·0					6·5
3,4–Xylenol	37·8	63·8	81·2	91·6	97·2	99·3	99·8	100·0			4·6
2–Ethylphenol	77·6	95·1	98·8	99·7	100·1						14
3–Ethylphenol	50·7	77·5	91·0	97·0	99·0	99·6	99·7				6·7
4–Ethylphenol	52·2	79·4	92·4	98·0	99·7	100·2					7·1
3–Methyl–5–ethylphenol	64·2	88·7	96·8	99·0	99·4						9·7
4–Indanol	32·8	57·3	74·7	87·2	94·6	98·5	99·5	99·8			3·8
5–Indanol	24·5	45·8	63·7	77·8	88·8	96·0	99·5	100·6			2·8
1–Naphthol	8·0	16·5	25·8	36·2	47·7	60·7	75·8	91·8	100·1		0·8–1·5
2–Naphthol	3·5	7·9	12·9	18·7	25·7	34·9	47·8	68·5	91·2	8·8	0·3–1·0
Catechol	0·2	0·4	0·6	0·9	1·2	1·7	2·6	4·3	8·4	91·6	0·02
3–Methylcatechol	0·7	1·6	2·6	3·7	5·2	7·3	10·7	17·4	35·5	64·5	0·07
4–Methylcatechol	0·4	0·8	1·3	1·9	2·8	4·0	5·9	9·5	19·8	80·2	0·04
Resorcinol	0·0	0·1	0·1	0·1	0·1	0·1	0·2	0·4	0·9	99·1	0·003

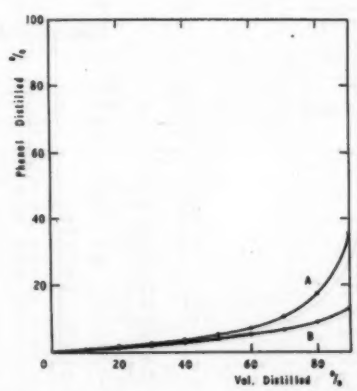
Values of n are again quoted in Table 5, but these are subject to greater variations from the mean than those from neutral or acid solutions, probably since the concentration of salt in the distilling flask increased throughout the distillation. This was especially apparent with the naphthols and dihydric phenols where an appreciable amount of the compound remained in the distilling flask towards the end of the distillation.

The phenomenon can be seen best in comparison of Figures 1 to 4 where the percentage of the phenol that distilled has been plotted against the percentage of solution that has been collected in the receiver. Figure 1 contains curves for phenol distilled from neutral and salt solutions. These curves have decreasing slopes as they approach the limit for the amount of phenol that can be distilled. All the monohydric phenols except the naphthols have similar curves. Dihydric phenols have distillation curves of the type shown in Figure 2, where 3-methylcatechol was distilled from neutral and salt solutions, the curves increasing in slope. The naphthols also possess this type of distillation curve when in neutral solution, but the effect of an increasing concentration of salt causes that for 2-naphthol (Figure 3) to assume an almost steady slope near the end of the distillation, whilst that for 1-naphthol (Figure 4) reverses its slope after the distillation of 70 per cent of the liquid from the flask.



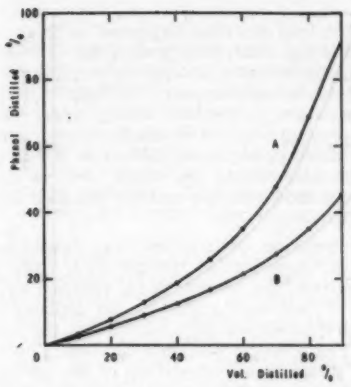
A Salt Solution. B. Neutral Solution.

FIGURE 1.—*Distillation of Phenol from Aqueous Solution.*



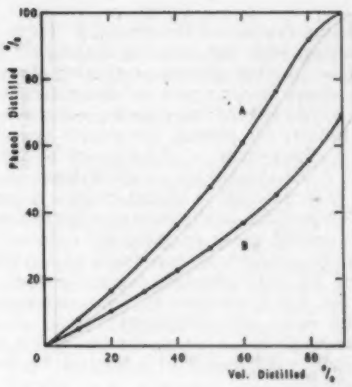
A. Salt Solution. B. Neutral Solution.

FIGURE 2.—*Distillation of 3-Methylcatechol from Aqueous Solution.*



A. Salt Solution. B. Neutral Solution.

FIGURE 3.—*Distillation of 2-Naphthol from Aqueous Solution.*



A. Salt Solution. B. Neutral Solution.

FIGURE 4.—*Distillation of 1-Naphthol from Aqueous Solution.*

(v) *Distillation at Constant Liquid Volume*

Using the determined n values from the previous sub-sections, it is possible to calculate the amount of a phenol that would distil from a solution the volume of which was kept constant throughout the distillation. For phenol and the cresols, values were obtained experimentally from acid and salt solutions, commencing the distillation as indicated above, but adding 25 ml of water to the flask after the collection of each 25 ml of distillate. The results are given in Table 6, the n values being determined from the equation

$$n = -2{\cdot}303 \log_{10} (1 - \frac{y}{100}) \frac{100}{x}$$

where (as before) x is the percentage of water that has distilled and y is the percentage of phenol that has then distilled. The values compare reasonably well with those quoted in Tables 4 and 5. In Table 6 is included also the result of an experiment in which phenol was steam distilled from acid solution when steam was passed through the solution by the normal method of steam distillation. Under these conditions, it was difficult to maintain a constant volume of liquid in the distilling flask, but values are not far different from those where water was added to the flask.

Evidently, a substantial error would appear in the determination of the phenols in ammoniacal liquors if the contents of the distilling flask were maintained at a constant volume, even in presence of salt, since it is unlikely that a volume of distillate greater than that originally in the distilling flask would normally be collected.

(vi) *Distillation from Alkaline Solution*

A number of monohydric phenols have been distilled in presence of alkali to determine the proportion of the phenol that might be lost during removal of the organic bases. The experiments were carried out in the same way as in sub-section (i), except that the 500 ml of phenol solution in the distilling flask contained 25 ml of 50 per cent sodium hydroxide solution. The results are given in Table 7, where it will be seen that, apart from phenol and 1-naphthol, the phenols are significantly volatile. The "*ortho*-effect" again plays an important part in the process. This is especially obvious with 2, 6-xylenol where approximately half the compound would be lost from solution if 90 per cent of the solution were evaporated. So far as ammoniacal liquors are concerned, phenol and the cresols are the most important constituents, and, save for *o*-cresol, there would be only a slight loss of these compounds in concentrating an alkaline solution. Thus, in an experiment where a solution of phenol was evaporated in presence of sodium hydroxide until salts separated, and the method followed that given by Key, except that 450 ml of solution was collected from 500 ml in the distilling flask, the recovery of phenol was determined to be above 98 per cent. Losses of *o*-cresol and the xylenols would, however, be appreciable.

TABLE 6.—*Distillation of Phenols with Constant Volume in Distilling Flask.*

Compound	Original Volume Distilled (per cent)																		n
	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	160	170	180	190	
	Phenol Distilled (per cent)																			
1	2																			3
Acid Solution																				
Phenol	19·9	36·0	48·8	59·2	67·5	74·0	79·2	83·6	86·9	89·3	91·8	93·8	95·5	96·7	97·6	98·2	99·0	99·5	99·8	2·2
Phenol, using steam	21·2	36·6	49·3	59·5	68·2	75·2	80·3	84·7	88·2	91·0	93·5	95·5								2·3
o-Cresol	42·8	66·7	80·7	88·8	93·6	96·5	98·2	99·0	99·5	99·8	100·0									5·5
m-Cresol	25·6	44·7	58·7	69·2	76·9	82·8	87·2	90·3	92·8	94·6	95·9	97·0	97·7	98·2	98·7					2·95
p-Cresol	26·2	45·1	59·3	69·7	77·6	83·4	87·8	91·0	93·4	95·2	96·4	97·4	98·1	98·6	99·0					3·0
Salt Solution																				
Phenol	25·4	44·0	57·9	68·2	76·2	81·8	86·2	88·8	91·8	93·6	94·9	95·8	96·6	97·0	97·3					2·9
o-Cresol	56·3	80·7	91·8	96·7	98·9	99·8	100·3													8·3
m-Cresol	35·3	57·9	72·5	82·0	88·3	92·4	95·2	96·9	98·0	98·7	99·0									4·3
p-Cresol	36·2	58·8	73·6	83·2	89·4	93·2	95·8	97·4	98·4	99·0	99·4									4·5

An interesting feature of the results in Table 7 arises in their comparison with the order of elution of the phenols by *cyclo*hexane from an alkaline stationary phase.[3] Taking the values where 90 per cent of the solution has been distilled as a measure of the relative volatilities, then the order is as follows for phenol, the cresols and xylenols:— 2,6-xylenol > 2,4-xylenol > 2,3-xylenol > 2,5-xylenol > *o*-cresol > 3,4-xylenol > 3,5-xylenol = *p*-cresol > *m*-cresol > phenol. This is almost exactly the same order as in the elution from a chromatographic column, except that *o*-cresol would there immediately follow 3,5-xylenol, and would show a significant resolution of 3,5-xylenol from *p*-cresol. Of the ethylphenols, the *ortho* compound has practically the same position in both sequences, though the *para* and *meta* were fractionally later in the steam distillation order than as column eluates. Both phenomena must be related to the degree of hydrolysis of the phenates in alkaline solution.

(vii) *Distillation of Oxidized Products of Dihydric Phenols*

Results in Tables 3 and 5 for dihydric phenols had shown that an appreciable proportion of the catechols would distil over with the monohydric phenols. Since there had been no previous indications from the literature that dihydric phenols were present in monohydric phenol distillates, it was decided to find out what happened to these compounds during the normal analytical procedure. It seemed fairly obvious that the dihydric phenols (especially catechols and quinols) would be substantially oxidized during the preliminary treatment to remove bases, where the alkaline solution is concentrated to a small volume, and that the resulting oxidized products would not be distilled in steam. Experiments were made in which the catechols were oxidized in alkaline solution and the solution then distilled after acidification.

Firstly, a solution of catechol was evaporated on the water bath in presence of sodium hydroxide until salts began to separate, the residue being acidified and made up to 500 ml. Salt was added in an amount such that, together with that formed on acidification, the total amount was 30 g. The solution was then distilled collecting 50-ml. fractions of distillate. Comparison of the optical densities of the fractions with those of catechol that had not been oxidized (Table 8) appeared to indicate either that the catechol had only been partly oxidized or that the oxidized products were steam-distillable. Moreover, agreement between duplicate experiments with the oxidized products was not very good. Experiments with oxidized 4-methylcatechol showed a similar behaviour, duplicate experiments being even less in agreement with one another.

TABLE 7.—*Distillation of Phenols from Alkaline Solution.*

Compound	Solution Distilled (per cent)										*n*
	10	20	30	40	50	60	70	80	90	In Residue	
	Phenol Distilled (per cent)										
1	2										3
Phenol	0·1	0·1	0·2	0·2	0·2	0·2	0·3	0·4	0·5	99·5	0·002
o–Cresol	0·6	1·0	1·4	2·0	2·5	3·1	3·7	4·3	6·5	93·5	0·04
m–Cresol	0·2	0·4	0·6	0·9	1·1	1·3	1·7	2·0	2·5	97·5	0·02
p–Cresol	0·3	0·5	0·8	1·0	1·2	1·5	1·8	2·2	3·0	97·0	0·02
2,6–Xylenol	1·6	3·2	4·9	6·7	9·0	11·6	15·6	22·6	49·5	50·5	0·14
2,5–Xylenol	0·7	1·4	2·1	2·9	3·7	4·5	5·5	6·9	10·2	89·8	0·06
2,4–Xylenol	0·5	1·1	1·7	2·5	3·3	4·3	6·0	9·1	21·2	78·8	0·05
2,3–Xylenol	0·6	1·3	2·1	3·1	4·1	5·2	6·4	7·8	11·1	88·9	0·06
3,5–Xylenol	0·3	0·5	0·7	0·9	1·1	1·4	1·8	2·2	3·5	96·5	0·02
3,4–Xylenol	0·2	0·4	0·5	0·7	0·8	1·1	1·5	2·1	4·3	95·7	0·02
2–Ethylphenol	0·8	1·6	2·3	3·1	3·9	4·8	5·9	7·4	11·3	88·7	0·06
3–Ethylphenol	0·4	0·7	1·0	1·2	1·4	1·6	1·8	2·2	3·0	97·0	0·02
4–Ethylphenol	0·3	0·5	0·7	1·0	1·3	1·6	1·9	2·3	3·4	96·6	0·02
4–Indanol	0·6	0·8	0·9	1·0	1·1	1·2	1·3	1·9	2·7	97·3	0·02
1–Naphthol									0·1	99·9	0·00

TABLE 8.—*Distillation of Catechols and Oxidized Catechols from Salt Solution.*

Compound	Method of Oxidation	Additions to Distilling Flask	Solution Distilled (per cent)								
			10	20	30	40	50	60	70	80	90
			Compound Distilled in Terms of Ultraviolet Absorbance (per cent)								
1	2	3	4								
Catechol	—	—	0·2	0·4	0·6	0·9	1·2	1·7	2·6	4·3	8·4
,,	—	$CaCO_3$	0·1	0·2	0·3	0·4	0·5	0·7	1·0	1·4	2·1
,,	—	$CaCO_3/PbCO_3$	nil	nil	nil	nil	nil	nil	nil	nil	nil
Oxidized Catechol	Evaporation of Alkaline Solution	—	0·1	0·2	0·4	0·6	0·8	1·0	1·5	2·7	5·4
,,	Shaking with Alkali (1 min.)	—	0·2	0·5	0·9	1·3	1·9	2·7	3·9	6·6	13·0
,,	,, (15 min.)	—	0·1	0·2	0·2	0·3	0·4	0·5	0·8	1·4	3·1
,,	,,	$CaCO_3$	0·1	0·2	0·3	0·4	0·6	0·8	1·1	1·8	3·3
,,	,,	$CaCO_3/PbCO_3$	nil	nil	nil	nil	nil	nil	nil	nil	nil
3-Methylcatechol	—	—	0·7	1·6	2·6	3·7	5·2	7·3	10·7	17·4	35·5
,,	—	$CaCO_3/PbCO_3$	nil	nil	nil	nil	nil	nil	nil	nil	nil
Oxidized 3–Methylcatechol	Shaking with Alkali	—	2·6	5·6	8·9	12·6	17·2	23·3	31·3	44·7	60·0
,,	,,	$CaCO_3/PbCO_3$	nil	nil	nil	nil	nil	nil	nil	nil	nil
4–Methylcatechol	—	—	0·4	0·8	1·3	1·9	2·8	4·0	5·9	9·5	19·8
,,	—	$CaCO_3/PbCO_3$	nil	nil	nil	nil	nil	nil	nil	nil	nil
,,	—	Acid/$PbCO_3$	0·3	0·6	1·0	1·5	2·2	3·1	4·7	7·7	17·5
Oxidized 4–Methylcatechol	Evaporation of Alkaline Solution	—	1·1	2·2	3·3	4·5	5·8	7·3	9·2	11·9	15·7
,,	Shaking with Alkali (1 min.)	—	2·4	4·9	7·8	11·1	14·9	19·6	25·6	34·4	44·8
,,	,, (15 min.)	—	0·3	0·5	0·8	1·1	1·4	1·9	2·6	4·2	7·4

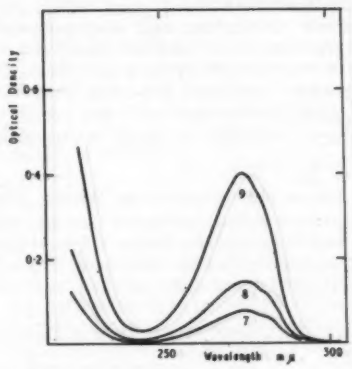
Further experiments in which catechol and 4-methylcatechol were oxidized by shaking an alkaline solution of the compound in presence of air, indicated that an increased time of oxidation produced a substance that was not so readily distilled in steam. The most interesting phenomenon was the production of a distillate with a substantially greater ultraviolet absorbance than that of the corresponding catechol. This has been observed with catechol and both its methyl homologues oxidized for short periods.

No detailed investigation has yet been made concerning the nature of the products formed on oxidation of catechols except that ultraviolet spectra of the steam-distillable oxidized products have been obtained and these have been compared with those of the original catechols. The corresponding spectra for catechol, 3-methylcatechol, 4-methylcatechol and their oxidized products are shown in Figures 5 to 10, the fraction numbers indicating which of the nine 50-ml fractions are present in each figure.

Comparison of Figures 5 and 6, for catechol and oxidized catechol, shows that the peak maximum moves from 2,750A to 2,800A on oxidation; and, whereas the ultraviolet absorption of catechol is negligible at 2,950A, that of the oxidized product is still appreciable at this wavelength. For oxidized catechol, the wavelength of the maximum optical density for the last fraction that distilled moved towards that of catechol, and probably resulted from the presence of a greater proportion of catechol in that fraction.

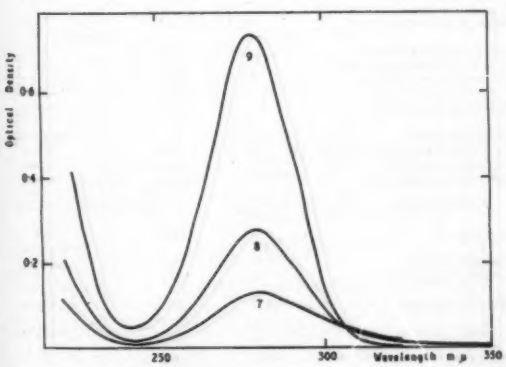
Figures 7 and 8 contain the ultraviolet spectra of distillate fractions for 3-methylcatechol and for its oxidized product. Here, the increase in optical density of the oxidized product at the higher wavelengths is even more apparent, and the spectrum runs at a higher level of absorbance into the visible region, the distillates appearing coloured. On the other hand, the absorption maximum of the oxidized product is at the same wavelength as that of 3-methylcatechol. Oxidation produces bands in the spectrum that appear as shoulders at about 2,950A and 3,150A. The absorption is also relatively high in the trough at 2,400A; the minimum optical density is 50A below that of 3-methylcatechol, and there is a decrease in optical density at shorter wavelengths. Again, there is an appearance of a proportion of unoxidized 3-methylcatechol in the later distillate fractions.

The ultraviolet spectra of 4-methylcatechol distillate fractions are given in Figure 9, and those of its oxidized product in Figure 10. The result of oxidization in this



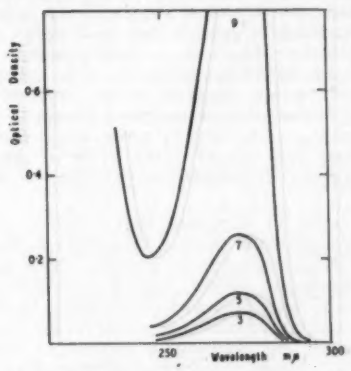
Fractions 7, 8, 9.

FIGURE 5.—*Ultraviolet Spectra of Catechol distilled from Aqueous Salt Solution.*



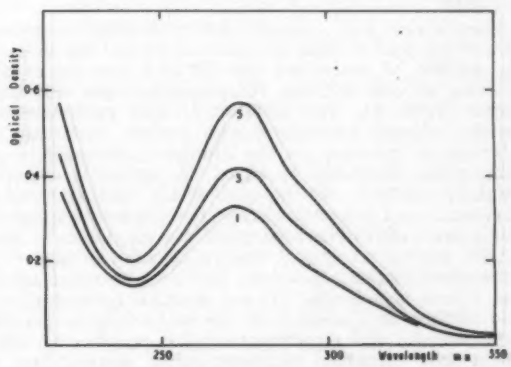
Fractions 7, 8, 9.

FIGURE 6.—*Ultraviolet Spectra of Oxidized Catechol distilled Aqueous Salt Solution.*



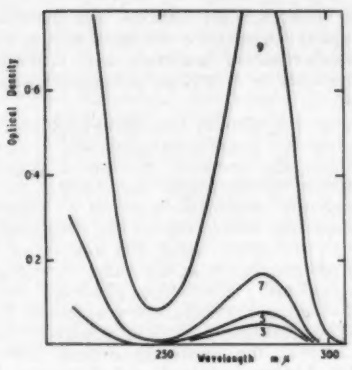
Fractions 3, 5, 7, 9.

FIGURE 7.—*Ultraviolet Spectra of 3-Methylcatechol distilled from Aqueous Salt Solution.*



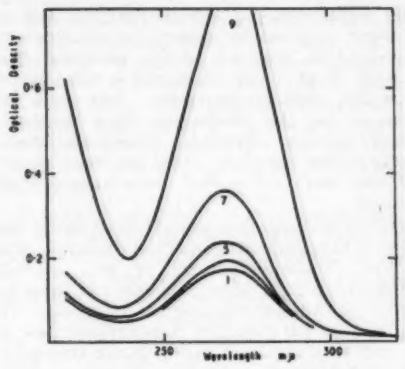
Fractions 1, 3, 5.

FIGURE 8.—*Ultraviolet Spectra of Oxidized 3-Methylcatechol distilled from Aqueous Salt Solution.*



Fractions 3, 5, 7, 9.

FIGURE 9.—*Ultraviolet Spectra of 4-Methylcatechol distilled from Aqueous Salt Solution.*



Fractions 1, 3, 5, 7, 9.

FIGURE 10.—*Ultraviolet Spectra of Oxidized 4-Methylcatechol distilled from Aqueous Salt Solution.*

case has been to shift the spectrum mainly to shorter wavelengths, and it thus differs from those of the other two catechols. Movement of the maximum is from 2,810A to 2,680 A, which is greater than with either catechol or 3-methylcatechol. There is a slight increase in optical density at the longer wavelengths. The position of the maximum of the last distillate of the oxidized product is again closer to that of the unoxidized catechol. No further information can at present be given about these oxidized products, and they should prove to be of interest in the study of chemical and biological oxidation of ammoniacal liquors.

At this point, it appeared that oxidized products of dihydric phenols would have a disturbing influence on the determination of monohydric phenols, particularly if they have a bromination value. Further investigation showed that they could be prevented from distilling by the presence of lead carbonate. As indicated earlier, in the present analytical procedure, the solution is neutralized with calcium carbonate to prevent distillation of thiocyanic acid, and lead carbonate is added to hold back any sulphide. It seemed possible that either, or both, of these compounds might suppress the distillation of the catechols, though it was impossible to predict their influence on the oxidized catechols.

Experiments with calcium carbonate alone in presence of catechol and of oxidized catechol showed that although the amount of compound that distilled was not as great as from an acid solution, the proportion was still appreciable (Table 8). The addition of lead carbonate to a solution already neutralized with calcium carbonate had a profound influence on the distillation, completely preventing the distillation both of the catechols and their oxidized products. In the case of the oxidized products of catechol and 3-methylcatechol, the first distillate fraction had a small ultraviolet absorption, the maximum at about 2,550A having an optical density of approximately 0·02. Subsequent factions, however, had no ultraviolet absorption at any wavelength. It was essential to neutralize an acid solution of a catechol for the lead salt to be effective; an experiment with 4-methylcatechol in presence of acid to which lead carbonate had been added showed that the catechol distilled to the same extent as when lead was absent.

In examination of the literature, there was no indication that the addition of calcium and lead carbonates would prevent distillation of dihydric phenols and their oxidized products, but it would seem to be very fortuitous that substances added for another purpose should solve an important problem of the analysis.

The presence of calcium and lead carbonate has but little effect on the steam distillation of the monohydric phenols. An experiment with *m*-cresol in presence of these compounds and salt indicated that the *m*-cresol could be quantitatively recovered, the result being practically identical with that in which *m*-cresol was distilled in presence only of salt.

(D) STEAM DISTILLATION OF ORGANIC BASES

Table 9 gives a list of the bases that have been determined in two ammoniacal liquors by Hughes[16] using solvent extraction to separate the bases from the liquors and gas-liquid chromatography for their subsequent deter-

TABLE 9.—*Bases in Ammoniacal Liquors.*

Compound	Concentration (p.p.m.)	
	Vertical Retort	Coke Oven
1	2	3
Pyridine	5·3	47·2
2-Methylpyridine	2·2	9·3
3-Methylpyridine	2·6	5·2
4-Methylpyridine	3·4	7·6
2,6-Dimethylpyridine	1·5	2·0
2,4-/2,5-Dimethylpyridine	2·7	5·0
2,3-Dimethylpyridine	0·9	2·5
3,5-Dimethylpyridine	0·7	2·5
3,4-Dimethylpyridine	trace	trace
2-Ethylpyridine	2·7	trace
2-Methyl-6-ethylpyridine	0·9	trace
2,6-Diethylpyridine	trace	trace
2,3,6-Trimethylpyridine	trace	trace
Total Pyridines	22·9	81·3
Aniline	13·5	11·8
2-Methylaniline	3·8	2·4
3-/4-Methylaniline	3·1	1·7
Dimethylanilines	trace	trace
Total Anilines	20·4	15·9
Quinoline	15·0	3·1
iso-Quinoline	12·7	2·4
Total Quinolines	27·7	5·5
Total Bases	71·0	102·7

mination. Compared with the total concentration of phenols in most ammoniacal liquors, they are relatively small in proportion, and in the determination of total monohydric phenols the possible error of 0·1 g/l. made by ignoring the presence of bases would not be significant. In addition to these bases, separations by column liquid—liquid chromatography have indicated the presence of indole in coke oven liquors, at concentrations up to about 50 p.p.m.

Steam distillation experiments have been made with some of these bases, and results are summarized in Table 10. The pyridines are readily distilled from neutral solution, though about 80 per cent of the solution must be distilled to recover the quinolines and aniline. All these bases appear to have salts that are more stable than those of the phenols. Indole is an amphoteric substance, but, whereas the presence of acid has little effect on its steam distillation, alkali clearly increases the rate of distillation.

The comparative stability of the sodium salts of the phenols, and the acid salts of the bases indicates that separation of the two groups of compounds would be more satisfactory by steam distillation from an acid solution than from alkaline solution.

(E) Suggested Changes in Analytical Procedure

The above investigation shows the alterations that should be made to improve the preliminary treatment of the sample for the determination of monohydric phenols. The two major items requiring modification are the evaporation of the liquor in presence of sodium hydroxide for the removal of bases, and the proportion of the liquid in the distilling flask that has to be collected in the distillation of the monohydric phenols.

It is suggested that the preliminary evaporation of the alkaline solution be discontinued, most especially to reduce consequent loss of phenols. Moreover, this procedure takes up the longest period of time in the whole analysis, about 2 to 3 hr being required for the evaporation: and, although constant attention is not required, it is necessary to maintain a certain amount of interest in the process, particularly towards the end. It is also difficult to stop the evaporation at exactly the same point on every occasion, and hence the proportion of liquid left at the end of the process will be a variable quantity. This could influence the final result, especially as the xylenols are appreciably steam volatile from alkaline media.

In the distillation of the phenols from aqueous solution, the constant, or intermittent, addition of water to the flask must be definitely eliminated from the procedure. Moreover, the volume of liquid in the distilling flask at the start should be measured with reasonable accuracy and a known amount of distillate be collected. Commensurate with a suitable degree of accuracy and convenience in operation, it should be sufficient to distil 90 per cent of the contents of the distilling flask when salt is present. Under these conditions, it is not strictly essential to add more water at this point in order that a volume of distillate may be collected equal to that originally in the distilling flask, as recommended in American practice.

The following is, then, the procedure that would be followed in the preliminary treatment of a sample of ammoniacal liquor for the determination of total monohydric phenols.

If cyanide were known to be present in the liquor, to 50 ml of the liquor would be added a few drops of ammonium polysulphide solution to convert the cyanide to thiocyanate, the reaction being allowed to proceed for about 15 min. An excess of lead carbonate would then be added to precipitate the polysulphide, which would be filtered from the solution. (Key [4].) With most liquors, cyanide is absent and the addition of polysulphide can be omitted. Sulphides are usually present in crude liquors and should be removed by the addition of lead carbonate followed by filtration. In spent liquors, sulphides are negligible in amount, and this stage can also be ignored.

Taking the sample of liquor as treated, or 50 ml of sample if the previous treatment was not necessary, it should be made slightly acid to "fix" any free ammonia, and water should be added to bring the volume to exactly 500 ml, the liquid being contained in a 1 litre distilling flask. To this solution, about 2 g of calcium carbonate should be added, followed by about 1 g of lead carbonate, and 30 g of sodium chloride. The solution should be distilled, collecting 450 ml of distillate, and making this volume up to 500 ml.

If bases are known to be present in amounts appreciably less than those of the phenols (e.g., less than about 5 per

TABLE 10.—*Distillation of Organic Bases.*

Compound	Conditions	Solution Distilled (per cent)										
		10	20	30	40	50	60	70	80	90	In Residue	*n*
		Base Distilled (per cent)										
1	2	3										4
Pyridine	Neutral Solution	80·5	96·1	99·3	99·9	100·0						15
"	HCl 1 : 500	0·3	0·7	1·0	1·3	1·6	1·9	2·3	2·8	3·5	96·5	0·03
"	HCl 1 : 20					0·1	0·1	0·1	0·1	0·3	99·7	0·001
"	H_2SO_4 1 : 50	0·1	0·1	0·2	0·2	0·2	0·2	0·3	0·3	0·3	99·7	0·003
2-Methylpyridine	Neutral Solution	89·9	98·8	99·9	100·0							21
"	H_2SO_4 1 : 50+Salt									0·2	99·8	0·001
Quinoline	Neutral Solution	43·8	69·7	84·0	92·8	97·0	99·0	99·7	100·0			5·2
"	H_2SO_4 1 : 50	nil	nil	nil	nil	nil	nil	nil	nil	nil	100·0	—
iso-Quinoline	Neutral Solution	36·5	61·3	77·7	88·1	94·3	97·7	99·2	99·8	100·0		4·2
"	H_2SO_4 1 : 50+Salt	nil	nil	nil	nil	nil	nil	nil	nil	nil	100·0	—
Aniline	Neutral Solution	44·8	71·9	86·7	94·3	98·0	99·4	99·8	100·0			5·6
"	H_2SO_4 1 : 50	nil	nil	nil	nil	nil	nil	nil	nil	nil	100·0	—
"	H_2SO_4 1 : 50+Salt	0·1	0·2	0·2	0·2	0·2	0·3	0·4	0·7	1·3	98·7	0·005
Indole	Neutral Solution	25·0	45·2	61·4	74·1	83·8	90·7	95·4	98·0	99·2	0·8	2·7
"	H_2SO_4 1 : 50	27·9	49·5	66·6	79·1	88·2	94·0	97·4	99·0	99·5	0·5	3·1
"	Alkaline Solution	40·7	67·4	84·3	93·9	98·1	99·5	100·0				5·1

cent), then the monohydric phenols may be determined in this distillate by bromination. Otherwise, the 450 ml of distillate should be made acid with 25 ml of 25 per cent sulphuric acid, and the volume made up to 500 ml. To this should be added 30 g of salt and the solution distilled as before, collecting 450 ml of distillate, which is made up to 500 ml, and monohydric phenols determined by bromination. The bases that are left with the residue in the distilling flask could be determined if desired. The bromination of phenols is considered in the Section IV.

IV BROMINATION OF MONOHYDRIC PHENOLS

(A) Methods in Use at the Present Time

The method used to determine the total amount of monohydric phenols in ammoniacal liquors, which does not require the provision of apparatus either to be specially provided for the purpose or expensive in cost, is based on the halogenation of the phenols. In most of the earlier work on liquor analysis, phenols were determined by iodination. This method was given in the first edition of "Gas Works Effluents and Ammonia"[4], and had been suggested in reports of the Alkali Inspectors.[8, 9] The practical disadvantage of the procedure was that the amount of sodium hydroxide that had to be present was dependent upon the amount of iodine that would be used, and it was, therefore, often necessary first to make a rough determination of phenols and then to add the correct amount of sodium hydroxide and repeat the determination.

In the second edition of Key's manual, the procedure suggested is to titrate a known portion of acidified steam distillate with 0·1 *N* bromate—bromide solution with frequent shaking until a yellow colour persists for 1 min. The excess of bromine is then determined by liberation of an equivalent amount of iodine on the addition of potassium iodide and titrating with sodium thiosulphate using starch as indicator. The same procedure is recommended by the Committee appointed by the Ministry of Health,[14] which suggests that the titration be carried out with the solution at a temperature of about 20°C.

In the method suggested by the above authorities, only a small excess of bromine is present at any time during and at the end of the reaction. The A.B.C.M.-S.A.C. Joint Committee,[15] on the other hand, recommends a procedure whereby a large excess of bromine is present throughout the reaction period. In this method, 200 ml of the sample (or 100 ml of stronger solutions) is placed in an iodine flask and 20 ml of 0·5 *N* bromate—bromide solution is added from a pipette. Then 10 ml of 25-per cent sulphuric acid is added and the neck of the flask sealed with 10 ml of 10-per cent potassium iodide solution. The flask is allowed to stand 1 hr in the dark at room temperature. The sealing solution is next washed into the flask and a further 10 ml of potassium iodide solution added. The iodine is titrated with 0·2 *N* sodium thiosulphate solution. In all cases, the result is expressed in terms of phenol.

(B) Discussion of the Method

Only the bromination method will be considered here. The method ascribed to Koppeschaar[17] ultimately depends upon a molecule of a phenol forming a halogenated derivative of a definite composition. Phenol itself, under varying conditions of reaction, always takes up three atoms of bromine to give the 2, 4, 6-tribromophenol. Six atoms of bromine are actually used up in the reaction since the displaced hydrogen combines with bromine to form HBr, and from this can be calculated the equivalent value used in the determination. For a solution containing only phenol, therefore, an accurate determination of its concentration could be made by bromination. Other phenols substituted only in *meta-* positions (e.g., *m*-cresol, 3, 5-xylenol and 3-ethylphenol) are said to behave similarly to phenol, taking up three atoms of bromine.[18] Even so, an error is introduced into the determination in the case of a mixture of these compounds since, although 1 ml of 0·1 *N* bromate—bromide solution is equivalent to 0·001567 g of phenol, it is also equivalent to 0·0018 g of *m*-cresol, and 0·00204 g of 3, 5-xylenol or 3-ethylphenol. Thus, to express the result of the determination of total monohydric phenols in a mixture in terms of phenol would yield a value below that actually present in the sample. In the worst instance, if mainly 3, 5-xylenol was present, the value would be some 20 per cent low.

An even greater error is produced by the presence of phenols that contain substituents, such as methyl groups in *ortho-* or *para-* positions, since they prevent the entry of bromine atoms at these positions. Hence, *o*-cresol and *p*-cresol theoretically should take up only two atoms of bromine, and 1 ml of 0·1 *N* bromate—bromide solution would be equivalent to 0·0027 g of either of these compounds, though the result would be recorded as 0·001567 g of phenol in the analysis.

A more important source of error has been a subject of much discussion in the literature[18 to 23], where it has been shown that phenols may brominate abnormally by taking up more bromine than would be expected theoretically for the number of free positions in the ring. Thus, Sprung[18] has obtained results that showed that *o*-cresol and *p*-cresol take up respectively about 2·2 and 2·3 atoms of bromine. This has been ascribed to the presence of an excess of bromine during the reaction period.[19] Ruderman[20] has shown that the degree of "over-bromination" is dependent upon the excess of bromine for *ortho-* and *para*-substituted phenols. Using a bromination time of 5 min., he found that above a 50 per cent excess of bromine there was no further increase in the over-bromination of *p*-cresol, the maximum value being 2·3 atoms of bromine absorbed per molecule of *p*-cresol; with *o*-cresol, the maximum was about 3·0 atoms of bromine per molecule, but only occurred when the excess of bromine was above 100 per cent. The author also indicated that if the time of bromination of *p*-cresol were increased beyond 5 mins. there was little further increase in the amount of bromine absorbed.

It will be recalled that two methods are in use at the present time for the determination of phenols by bromination: one in which there is only a small excess of bromine present, and the second in which there is a substantial excess of bromine present throughout the reaction period; thus, the two methods may be expected to give different results.

The work of Francis and Hill[19] would indicate that the titration to a small excess of bromine, as used by Key, should lead to each phenol taking up its theoretical amount of bromine, whereas in the method of the A.B.C.M.-S.A.C. Joint Committee overbromination of a number of phenols would occur with the absorption of excess bromine. However, although the method given by Key and by the Committee appointed by the Ministry of Health would appear to yield theoretically correct results, from a practical point of view the other method would seem to be more satisfactory. Thus, in the first procedure, bromine is being

constantly produced in a vessel that has to be open to the atmosphere, though it is possible that loss by volatilization would only become appreciable towards the end of the titration. Moreover, two titrations are required in this method, the result involving four burette readings, with a consequent increase in error in the determination. In the excess bromination procedure, such errors will be of smaller importance, since all the solutions required in the reaction are in a stoppered bottle, except the acid; the latter can be added quickly since an accurate measure of its volume is not necessary, and the bottle can then be closed quickly before much bromine is liberated. There is then only one titration to be performed, which can be made sufficiently large to reduce the degree of error. The extent of overbromination of each compound must, however, be determined.

It will be clear that, whichever of the two methods is used, a substantial error in the result will appear unless the correct factor is chosen to relate the titration to the concentration of total phenols in solution. This requires a prior knowledge of the ratio of the phenols present in the sample, and of their individual bromination values. In the case of ammoniacal liquors, a fairly detailed survey of the phenolic contents of various types of liquors has already been made using a chromatographic process.[3] Employing these results to devise a method for determination of total phenols by ultraviolet spectrophotometry showed that a factor could be obtained to relate the ultraviolet absorption of the liquor to the total concentration of phenols present, the value being reasonably constant for a given type of liquor, and in fact did not vary greatly with different types of liquors. It thus seemed possible that a similar factor could be calculated for the bromination of phenols in liquors, provided that the bromination values of all the phenols were known. Theoretically, these bromination values are known, but in the case of excess bromination they must be determined for standard conditions.

The object of the present investigation has been to determine these bromination values and to combine them with the results of the chromatographic analysis of liquors to find the bromination factor for each liquor. Since the excess bromination method had been in use for some time in our laboratories, the experiments were made under these conditions.

(c) Determination of Bromination Values of Monohydric Phenols

(i) *Experimental*

A number of monohydric phenols known to be present in ammoniacal liquors have been brominated under conditions where overbromination was possible, and the number of bromine atoms absorbed in periods of time from 1 to 120 min. have been determined.

Bromination was carried out in bottles of capacity 350 ml that had well-fitting ground glass stoppers. The pure phenols were accurately weighed to give solutions of concentration approximately 1 g/l. Then 10 ml of the solution was placed in the bottle and 40 ml of water added; this was followed by 20 ml of 0·1 N potassium bromate—bromide solution. Next, 10 ml of 25-per cent sulphuric acid was poured in quickly from a measuring cylinder and the stopper of the bottle immediately inserted. The bottle was shaken for a period of 2 min. For reaction periods greater than 5 min., the bottle was placed in the dark for the requisite length of time. The reaction was arrested by the addition of 5 ml of 10-per cent potassium iodide solution, and the liberated iodine titrated with 0·1 N sodium thiosulphate solution using a calibrated burette. Since the bromate—bromide solution contained an accurately weighed amount of potassium bromate, this was used as a standard to check the normality of the thiosulphate solution, the standardization being made in the same way as the bromination experiments, but with 50 ml of water present.

(ii) *Results*

The results of these bromination experiments are given in Table 11 and are quoted to two decimal places, though the accuracy to the second place is not warranted. The

TABLE 11.—*Atoms of Bromine Absorbed per Molecule of Phenol.*

Compound	Time (min.)					
	1	5	15	30	60	120
1	2					
Phenol	2·99	3·02	3·02	3·02	3·04	3·05
o-Cresol	2·21	2·78	3·19	3·30	3·36	3·46
m-Cresol	2·90	2·97	3·07	3·10	3·19	3·27
p-Cresol	2·02	2·21	2·30	2·41	2·45	2·49
2,6-Xylenol ..	2·45	2·58	2·62	2·65	2·62	2·67
2,5-Xylenol ..	2·19	2·48	2·90	3·18	3·21	3·29
2,4-Xylenol ..	1·92	2·03	2·09	2·09	2·18	2·28
2,3-Xylenol ..	2·11	2·42	2·86	3·07	3·13	3·20
3,5-Xylenol ..	2·80	3·27	3·29	3·34	3·44	3·35
3,4-Xylenol ..	1·89	2·16	2·45	2·61	2·66	2·89
2-Ethylphenol ..	2·04	2·25	2·54	2·93	3·16	3·27
3-Ethylphenol ..	2·90	2·95	3·00	3·00	3·11	3·41
4-Ethylphenol ..	2·01	2·31	2·61	2·84	3·23	3·56

values are plotted as curves in Figs. 11 to 14. It is apparent that all the phenols have absorbed almost immediately the theoretical amount of bromine, usually two or three atoms, only a few compounds having values a little below the theoretical after a reaction time of 1 min. Afterwards, there is a slow increase in absorption of bromine above the theoretical value with increasing time of contact. This rate of increase appears to be least with those phenols that have already taken up three atoms of bromine, and is especially noticeable with phenol, the curve of which is probably a straight line of zero slope within the limits of experimental error, indicating that there is practically no overbromination of phenol.

The addition of alkyl groups seems always to produce overbromination of phenols, and this is apparent even amongst compounds substituted only in *meta* positions. The *meta*-substituted phenols (e.g., *m*-cresol, 3,5-xylenol and 3-ethylphenol) have absorption—time curves in which the slope does not appreciably alter. Some of the other curves show an obvious change of gradient during the first 30 min. of the reaction, especially *o*-cresol, 2,3-xylenol 2,5-xylenol, 2-ethylphenol and 4-ethylphenol. Subsequently, these curves become straight lines with gradients similar to those of the *meta*-substituted phenols, although some (particularly 4-ethylphenol) show a relatively steep gradient.

Most of the phenols gave precipitates on reaction with bromine, though the bromo-compounds of *o*-cresol, 2,6-xylenol and 2,4-xylenol were soluble in the reaction medium. With *o*-cresol, a precipitate that was formed almost immediately soon disappeared; it reappeared shortly afterwards, and finally dissolved completely.

In the final titration, the end-point is a change from blue to colourless. It was observed that, after the titration, the blue colour had a tendency to return fairly quickly with some phenols, especially with *o*-cresol, *m*-cresol, 3,5-xylenol and 2-ethylphenol. With most other compounds, the reappearance of blue colour was less rapid, the slowest rate being with *p*-cresol and 2,6-xylenol. It was further noticed that the return of the blue colour had frequently a connexion with the time of the bromination reaction: the greater this time was, the faster the blue colour returned.

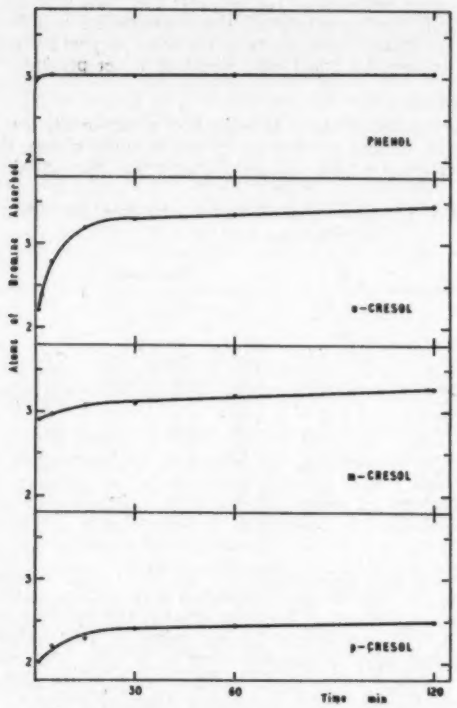


FIGURE 11.—*Bromination of Phenol and the Cresols.*

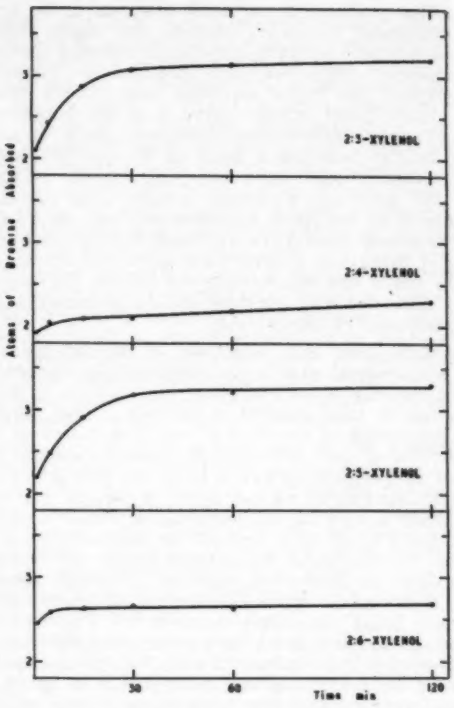


FIGURE 12.—*Bromination* of 2, 3-, 2, 4-, 2, 5- and 2, 6-*Xylenols.*

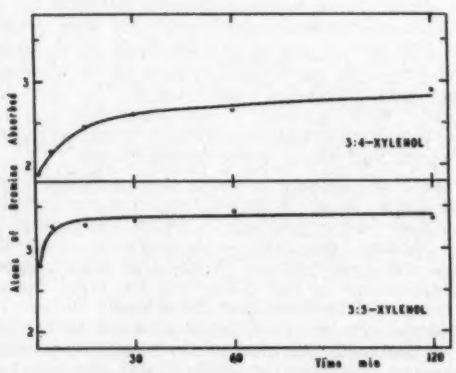


FIGURE 13.—*Bromination of* 3, 4- *and* 3, 5-*Xylenols.*

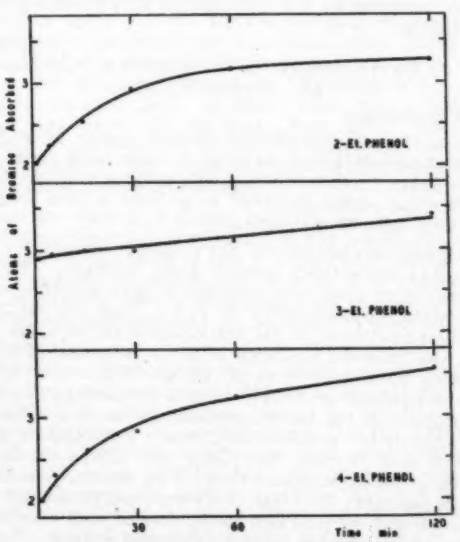


FIGURE 14.—*Bromination of Ethylphenols.*

An interesting phenomenon occurred with 3,4-xylenol and 3-ethylphenol. At times longer than 15 min. with 3,4-xylenol, and in the 120-min. reaction with 3-ethylphenol, a number of black specks were observed in the liquid at the end of the titration. These soon imparted a blue colour to the solution, which required the addition of more thiosulphate solution to discharge it. For this reason, it was difficult to assess accurately the final end-point of the titration, and a significant error appeared in these results. This can be seen with 3-ethylphenol (Table 11) which shows only a gradual rise during the first 60 min., but a substantial one after 120 min.

The return of the blue colour may have some connexion with the overbromination of phenols, since, if the bromine that is absorbed above the theoretical amount is attached to the molecule by relatively weak forces, it might conceivably be slowly released into the solution. Although the overbromination of phenols could in some instances be an adsorption phenomenon, it is possible that a more powerful bond could exist between the bromine and the bromo-compound, even to the extent of bromination of the alkyl group, or by attachment at some other position in the molecule.

A further observation is concerned with the dilution of the reaction medium. In Section c(i) above, 10 ml of the phenol solution was used and 40 ml of water added to it. With 90 ml of water present, it was found that there was no difference in the final result in the case of phenol, though the precipitate took a longer time to appear (over 1 min. as against 20 sec. with 40 ml of water). In presence of 190 ml of water, no satisfactory result could be achieved, since the bromine was liberated only slowly from the acidified bromate—bromide solution and less than the theoretical amount was released.

Some experiments were carried out with phenol and *o*-cresol involving titration with bromate—bromide solution, and then titrating the excess after the appearance of a yellow colour. It was found to be very difficult to attain reproducible results by this method, especially for *o*-cresol. A substantial excess of the bromate—bromide solution appeared to be necessary at the end-point of the first titration to achieve a theoretical result. Using a calculated small excess (1 ml) of bromate—bromide solution with phenol, a reaction time of 4 min. was required; with a 5 ml excess, the time was about 2 min. Results were frequently below the theoretical amount for *o*-cresol, even with an appreciable excess of bromine and slow titration. A more detailed investigation of this method is required to assess its accuracy and limitations.

It is clear that rigorously standard conditions must be used in the determination of phenols by bromination. Although the addition of a large excess of bromine can lead to overbromination of phenols, under standard conditions of concentrations and time of reaction the same amount of bromine should always be taken up by a given phenol. The reaction curves indicate that a time of 30 or 60 min. would be the best.

(D) Calculation of a Bromination Factor for Ammoniacal Liquors

Accepting that the determination will involve the excess bromination method, the amount of bromine that would be absorbed by the total amount of monohydric phenols in samples of 30 ammoniacal liquors has been calculated from the concentration of each phenol in a liquor, obtained by chromatographic analysis, and from the amount of bromine used in the bromination of each phenol.

It was decided that the period of bromination would be either 30 or 60 min., and values were calculated for both these times to determine the extent of the difference. The figures in Table 11 are quoted in terms of atoms of bromine absorbed by 1 molecule of the phenol. For the calculation, it was necessary to convert this figure to grams of bromine absorbed by 1 gram of the phenol, and then double the result to give the grams of bromine used in the reaction with 1 gram of a phenol. The values calculated in this way are included in Table 12; they are not always exactly equivalent to the values for 30 and 60 min. in Table 11, since the experimentally determined figures are not used, but values were taken from graphs, such as those in Figures 11 to 14. The difference was not usually greater than 1 per cent. The value for phenol from the graph was 5·14; the theoretical value for 6 atoms of bromine is 5·10. In the chromatographic analysis of phenols in ammoniacal liquors, it was not possible to obtain a complete separation of the xylenols and ethylphenols, and hence average values for groups of these compounds had to be used. These values are included in Table 12, the different combinations being necessary since not all the liquors were analysed in the greatest possible detail.

The values involved in the calculations are given in Table 13. The third section of Table 13 gives the concentration of the different phenols determined using chromatography. A number of these results have appeared in an earlier Gas Council *Research Communication*[3], but some others have also been included. The fourth and fifth sections of Table 13 show the bromination figures for 30 and 60 min. respectively. In each of these sections, the total bromine absorbed in the reaction has been divided by the total concentration of phenols (from section 3 of Table 13) to give the figure for grams of bromine absorbed per 1 gram of total monohydric phenols in the liquor. The results are in the final columns of sections 4 and 5 and form the important part of Table 13. The liquors have been arranged in groups, the order of the groups being roughly one of decreasing bromination values. It will be seen that this has resulted to some extent in liquors coming lower in Table 13 when they are produced under conditions where greater amounts of low-temperature products leave the gas-making plant. In such liquors, there is a larger proportion of alkylphenols which have lower bromine values.

A satisfactory feature of the results is that all the values lie within a fairly narrow range, whilst values for liquors from the same type of carbonization system fall within

Table 12.—*Bromination Values Used in Calculations.*

Compound	Grams of Bromine Consumed/Gram of Phenol	
	30 min.	60 min.
1	2	3
Phenol	5·14	5·14
o-Cresol	4·88	4·98
m-Cresol	4·62	4·70
p-Cresol	3·56	3·62
2,6-Xylenol	3·48	3·48
2,5-Xylenol	4·16	4·22
2,4-Xylenol	2·78	2·86
2,3-Xylenol	4·04	4·10
3,5-Xylenol	4·36	4·38
3,4-Xylenol	3·44	3·48
2-Ethylphenol	3·82	4·14
3-Ethylphenol	3·98	4·08
4-Ethylphenol	3·74	4·22
Mixtures :—		
Total Xylenols	3·74	3·89
2,3-, 2,4-, 2,5- 2,6-Xylenols + 2-Ethylphenol	3·66	3·76
3,4-, 3,5-Xylenols + 3-, 4-Ethylphenols	3·88	4·04
2,3-, 2,4-Xylenols + 2-Ethylphenol	3·55	3·70
2,3-, 2,4-, 2,5-Xylenols + 2-Ethylphenol	3·70	3·83
3,4-Xylenol + 4-Ethylphenol	3·59	3·85
3,5-Xylenol + 3-Ethylphenol	4·17	4·23

TABLE 13.—*Determination of Bromination Factors for Ammoniacal Liquors.*

No.	Type of Liquor		Concentration of Phenol (g/l)										Bromine Consumed (g)											
													30 min.										60 min.	
			A	B	C	D	E	F	G	H	J	Total	A	B	C	D	E	F	G	H	J	Total	per g Total Phen'ls	Total	per g Total Phen'ls
1	2		3										4											5
1	Coke Oven		1·36	0·15	0·37	0·18		0·07		0·06		2·19	6·98	0·73	1·71	0·64		0·26		0·23		10·55	4·82	10·62	4·85
2	,, ...		1·42	0·10	0·28	0·14		0·05		0·03		2·02	7·28	0·49	1·29	0·50		0·18		0·12		9·86	4·88	9·92	4·91
3	,, ...		0·45	0·06	0·12	0·06		0·04		0·02		0·75	2·31	0·29	0·55	0·21		0·15		0·08		3·59	4·77	3·62	4·83
4	,, ...		1·29	0·11	0·29	0·14		0·04		0·02		1·89	6·63	0·54	1·34	0·50		0·15		0·08		9·24	4·89	9·28	4·92
5	,, ...		0·77	0·15	0·22	0·14		0·07		0·03		1·38	3·96	0·73	1·01	0·50		0·26		0·12		6·58	4·78	6·63	4·81
6	,, ...		0·64	0·05	0·16	0·07		0·04		—		0·96	3·29	0·24	0·74	0·25		0·15		—		4·67	4·87	4·69	4·88
7	,, ...		0·86	0·11	0·24	0·10		0·07		0·06		1·44	4·43	0·54	1·11	0·36		0·26		0·23		6·93	4·82	6·97	4·84
8	,, ...		0·94	0·12	0·26	0·11		0·07		0·05		1·55	4·83	0·59	1·20	0·39		0·26		0·19		7·46	4·82	7·51	4·84
9	,, ...		0·78	0·07	0·19	0·09		0·04		0·02		1·19	4·01	0·34	0·88	0·32		0·15		0·08		5·78	4·86	5·81	4·88
10	,, ...		0·98	0·10	0·22	0·12		0·04		0·02		1·48	5·03	0·49	1·02	0·43		0·15		0·08		7·20	4·86	7·22	4·87
11	,, ...		1·59	0·25	0·39	0·22		0·11		0·05		2·61	8·17	1·22	1·80	0·78		0·40		0·19		12·56	4·82	12·66	4·85
12	,, ...	Spent	0·59	0·04	0·11	0·05		0·02		—		0·81	3·03	0·20	0·51	0·18		0·07		—		3·99	4·92	4·01	4·94
13	Horizontal Retort ..		1·14	0·18	0·26	0·15		0·12		0·03		1·88	5·85	0·88	1·20	0·53		0·44		0·12		9·02	4·80	9·08	4·83
14	Intermittent Verticals	Retort House	2·91	0·50	0·83	0·57	0·06	0·17	0·08	0·09	0·10	5·31	14·96	2·44	3·83	2·03	0·21	0·60	0·33	0·32	0·42	25·14	4·73	25·36	4·78
15	,,	Condenser	3·43	0·69	0·87	0·57	0·07	0·17	0·05	0·10		5·95	17·63	3·36	4·02	2·03	0·24	0·60	0·21	0·39		28·48	4·78	28·71	4·82
16	,,	Crude	2·27	0·53	0·57	0·39	0·04	0·17	0·04	0·06		4·07	11·67	2·59	2·63	1·39	0·14	0·60	0·17	0·23		19·42	4·78	19·58	4·82
17	Low Temperature ..		3·79	0·85	0·95	0·72	0·15	0·33	0·13	0·16	0·19	7·27	19·48	4·15	4·38	2·56	0·52	1·17	0·54	0·57	0·79	34·16	4·71	34·50	4·75
18	Continuous Verticals	Crude	2·32	0·54	0·65	0·49		0·35		0·15		4·50	11·92	2·64	3·00	1·74		1·28		0·58		21·16	4·70	21·36	4·74
19	,,	,,	2·45	0·89	0·75	0·60		0·42		0·13		5·24	12·60	4·35	3·46	2·14		1·54		0·50		24·59	4·69	24·84	4·74
20	,,	,,	2·86	0·85	0·71	0·55	0·08	0·22	0·10	0·07	0·11	5·55	14·70	4·15	3·28	1·96	0·28	0·78	0·42	0·25	0·46	26·28	4·73	26·51	4·77
21	,,	Retort House	2·03	0·39	0·59	0·47	0·05	0·16	0·07	0·09	0·08	3·93	10·43	1·90	2·72	1·67	0·17	0 57	0·29	0·32	0·33	18·40	4·68	18·60	4·73
22	,,	,,	1·84	0·43	0·57	0·42	0 08	0·16	0·08	0·15		3·73	9·46	2·10	2·63	1·49	0·28	0·57	0·33	0·58		17·44	4·68	17·62	4·73
23	,, ..	Hot Gas Electro-Detarred	2·67	1·22	0·85	0·67	0·16	0·42	0·09	0·16		6·24	13·73	5·95	3·92	2·38	0·56	1·49	0·37	0·62		29·02	4·66	29·37	4·71
24	,, ..	,,	3·37	1·27	1·06	0·84	0·12	0·31	0·15	0·10	0·08	7·30	17·32	6·19	4·88	2·99	0·42	1·10	0·62	0·36	0·33	34·21	4·68	34·60	4·74
25	,,	Spent	2·22	0·61	0·74	0·56	0·07	0·22	0·10	0·07	0·12	4·71	11·41	2·98	3·41	1·99	0·24	0·78	0·42	0·25	0·50	21·98	4·67	22·22	4·72
26	"Rexco"		1·28	0·31	0·44	0·33		0·29		0·12		2·77	6·57	1·51	2·03	1·18		1·06		0·47		12·82	4·63	12·95	4·68
27	Lurgi	Tar Liquor	1·23	0·44	0·55	0·29			0·48			2·99	6·32	2·15	2·54	1·03			1·80			13·84	4·63	14·02	4·69
28	,, ...	,,	1·60	0·46	0·74	0·53	0·07	0·34		0·14	0·18	4·06	8·22	2·25	3·42	1·89	0·24	1·26		0·50	0·75	18·53	4·57	18·76	4·62
29	,, ...	Oil Liquor	2·01	0·89	0·77	0·49			0·49			4·65	10·33	4·34	3·56	1·74			1·83			21·80	4·69	22·06	4·74
30	,, ...	,,	2·34	1·01	1·05	0·71	0·17	0·52		0·14	0·18	6·12	12·03	4·93	4·85	2·53	0·59	1·92		0·50	0·75	28·10	4·59	28·46	4·65

Key to columns in Sections 3 and 4 :—

A Phenol
B *o*–Cresol
C *m*–Cresol
D *p*–Cresol
E 2,6–Xylenol
F 2,4–, 2,3–Xylenols, 2–Ethylphenol
G 2,5–Xylenol
H 3,4–Xylenol, 4–Ethylphenol
J 3,5–Xylenol, 3–Ethylphenol

Columns A to J have been omitted from Section 5.

even closer limits. It is also interesting that variations in plant operation and the point of origin of the liquor from a given type of process have little effect on the bromination figure, thus the coke oven liquors were produced under a variety of different conditions, and those from continuous-vertical retorts came from different parts of the plant in such Works.

The results of Table 13 have been averaged under process groups in Table 14. There, in col. 5 and 6 are the factors that would be used in a determination by bromination to convert the amount of 0·1N bromate—bromide solution consumed to the total amount of monohydric phenols. For a given type of liquor the values for 30 and 60 min. never differ by more than about 1 per cent; hence the bromination time within this period is not very critical and there is no reason why 30 min. should not be taken as a standard time.

TABLE 14.—*Averages of Bromination Factors.*

Type of Liquor	Number in Average	Grams of Bromine/Gram of Total Phenols		Grams of Phenols ≡ 1ml 0·1N KBr O_3	
		30 min.	60 min.	30 min.	60 min.
1	2	3	4	5	6
Coke Oven	12	4·84	4·81	0·00165	0·00164
Horizontal Retort ..	1	4·80	4·83	0·00167	0·00166
Intermittent Verticals	3	4·76	4·81	0·00168	0·00166
Low Temperature ..	1	4·71	4·75	0·00170	0·00168
Continuous Verticals	8	4·69	4·74	0·00170	0·00169
"Rexco"	1	4·63	4·68	0·00173	0·00171
Lurgi	4	4·62	4·68	0·00173	0·00171
Average for All Groups				0·00169	0·00168
Value in Use.. ..				0·001567	

Considering next the factors for different types of liquors, there are some significant differences between the values but it would be more convenient if they could be combined into fewer groups. It is considered that two factors could be selected to cover the whole range of liquors: one involving coke ovens and horizontal retorts, which consist of processes where there is considerable thermal cracking, and the other involving all other types. The values would be respectively 0·00165 and 0·00170. Alternatively, with a slightly increased degree of error, a value of 0·00169 could be used if the type of liquor were not known.

These values are significantly higher than the value at present in use, where the phenols are returned in terms of phenol (C_6H_5OH). If the value of 0·00157 has been used with the overbromination technique, then it may be expected that results have been some 7 per cent below that for the correct total amount of monohydric phenols.

(E) PROPOSED METHOD

In the absence of a more detailed investigation, it is not possible here to decide which is the better of the two methods of bromination. Since only the overbromination method has been examined in detail and factors derived for it, then this must be the one proposed.

Taking the steam distillate produced as in Section III(E), 50 ml of the solution should be put into a 350-ml bottle with a well-fitting ground glass stopper, followed by 20 ml of 0·1 N potassium bromate—bromide solution. Then 10 ml of 25-per cent sulphuric acid should be poured in quickly from a measuring cylinder and the stopper of the bottle immediately replaced. The bottle should be shaken for 2 min. and allowed to stand in the dark. The temperature throughout should be about 20°C. After 30 min., 5 ml of 10-per cent potassium iodide solution should be added and the solution titrated with 0·1 N sodium thiosulphate solution, with starch as indicator. The total concentration of monohydric phenols in g/l (c) in the original sample is then given by

$$c = f.\frac{x}{y}$$

where x is the volume of bromate—bromide solution consumed (ml), y is the volume (ml) of the original sample in 50 ml of distillate, and f the bromination factor, which should be

1·65 for coke oven and horizontal retort liquors, or

1·70 for other types.

Using this procedure, results have been found to agree quite well with those determined by ultraviolet spectrophotometry.

V PERMANGANATE VALUES OF AMMONIACAL LIQUORS

(A) INTRODUCTION

In addition to the determination of the amounts of different constituents in an ammoniacal liquor, it is normal practice to measure the "Permanganate Value". The result obtained is a figure representing the amount of oxygen absorbed by the liquor from N/80 acid potassium permanganate in a period of 4 hr at 27°C, and is quoted in terms of parts of oxygen absorbed per 1 mill. parts of liquor. Depending on the type of liquor, the value will normally be found in the range 2,000 to 25,000 p.p.m. The constituents of liquors that consume the oxygen are some inorganic anions (sulphides, thiosulphate and thiocyanate) and organic compounds (mainly the phenols). The amount of oxygen absorbed per 1 gram of a liquor constituent is between about 0·5 and 2 g, and appears nearly always to be less than the amount that can be postulated by complete oxidation to products such as CO_2, H_2O and SO_4. It is not proposed to consider here the merits and disadvantages of the test, or to compare it with other ways of chemical oxidation, since it has become the chief means of measuring the polluting characteristics of ammoniacal liquors, and in the past has invariably been quoted in their analyses.

In addition to the determination of the total permanganate value of a liquor, it is usual to assess the contributions of the major constituents to the total, which can be obtained from their determined concentrations and their individual permanganate values. The accepted permanganate values for such constituents are due to Frankland and Silvester[24], and to Linder[9], and are shown in Table 15. The permanganate value for monohydric phenols is the

TABLE 15.—*Permanganate Values at Present Accepted.*

Constituent	Measured As:	Permanganate Value (Grams of Oxygen/Gram of Constituent)	Reference
1	2	3	4
Sulphide	H_2S	1·345	9
Thiosulphate	S	0·856	24
Thiocyanate	CNS	0·827	24
Phenol	C_6H_5OH	1·780	24

least satisfactory figure if calculated from the factor in Table 15 together with the factor that is at present accepted for their bromometric determinations, since both have been determined for phenol and not for the mixture of monohydric phenols present in the liquor. A more accurate measure of the permanganate value for monohydric phenols can be obtained directly on the steam distillate produced for determination of their total amount by bromination.

The sum of the permanganate values for sulphide, thiosulphate, thiocyanate and monohydric phenols is then subtracted from the total determined permanganate value and results in the so-called " difference figure ". The difference arises from constituents in the liquor that have permanganate values and that are not determined in the analysis. The major contribution is from the dihydric phenols; minor contributions will be from some bases (anilines), neutral bodies, and constituents not identified (such as oxidation products of the dihydric phenols) together with the errors in the determinations (particularly in that of sulphides).

As a result of the chromatographic analysis of ammoniacal liquors, it has now been possible to assess the contribution of the dihydric phenols to the permanganate value. This has required the determination of their individual permanganate values. At the same time, values have been obtained for a number of monohydric phenols in order to produce a more realistic value for the calculated permanganate value due to total monohydric phenols.

The permanganate values for the inorganic anions have been checked and have shown some discrepancies from values at present accepted. In this respect, if reference is made to the publications of the Alkali Inspectors[9], it will be found that the conditions specified for the test are substantially different from those now employed. In particular, the amount of permanganate was not standard for every test, it being suggested that 25 ml (or more) be employed with spent liquors and 45 to 50 ml with liquors containing sulphide. Different volumes of sample were used in the determination, and, whereas now 100 ml would be the total volume of sample plus water, the volume of added water was then 250 ml. Hence, it is possible that permanganate values given in Table 15 might not apply to determinations now made by the procedure of the Ministry of Health Committee where the permanganate is present in greater concentration throughout the reaction period. Frankland and Sylvester[24] give no details of the procedure used to determine the permanganate values of pure compounds, but state that they were " made on exactly the same lines as in the ordinary method of sewage analysis ". Linder[9] determined the permanganate value of sulphide under the conditions quoted by the Alkali Inspectors, and showed that a higher value (H_2S = 1·45) was obtained for this ion in the 3-min. determination where the conditions for this test were then different from those for the 4-hr test (H_2S = 1·345), the concentration of permanganate being about twice as great in the 3-min. test than in the longer test.

(B) Experimental Procedure

Since the procedure has now become well established, and as the test is an empirical one, the conditions used were those given by the Ministry of Health.[14] The A.B.C.M.-S.A.C. Joint Committee[15] gives a procedure that is identical with that of the Ministry of Health. The method given in the second edition of Key[4] has been taken from the 1929 edition of the Ministry of Health's publication, the procedure being given in less detail than in the other publications, the major difference being that the concentration of sulphuric acid is twice that quoted by the Ministry of Health.

For the present determinations on the phenols, a solution of the phenol in water of concentration about 1 g/l was accurately made up, then diluted 10 times, and 10 ml of the latter solution used in the test. With the less soluble phenols and those available only in small amounts, the more dilute solution was made up directly from the weighed sample. Solutions of dihydric phenols were stabilized by the addition of acid, whilst a few of the more complex monohydric phenols required the addition of a small quantity of sodium hydroxide to facilitate their solution.

The 12 oz glass-stoppered bottles, used in the test, each contained 10 ml of 25-per cent (v/v) sulphuric acid, 50 ml N/80 potassium permanganate, 90 ml water, and 10 ml of the phenol solution; " blank " determinations contained 100 ml of water. The solution was at 27°C. before the addition of the phenol solution. After 4 hr in the water bath at 27°C, 5 ml of 10-per cent potassium iodide solution was added and the iodine titrated with N/80 sodium thiosulphate solution, the consumption of permanganate being between about 10 and 15 ml. The thiosulphate solution was made up each day from a stock N/4 thiosulphate solution and standardized each time against a standard potassium iodate solution. A calibrated burette was used in all determinations.

It was found that an error could arise in the standardization procedure given in the Ministry of Health's publication[14], where it is stated that into a glass-stoppered bottle are placed 5 ml potassium iodide solution, 10 ml of 25-per cent sulphuric acid, and 25 ml. N/40 iodate solution *in that order*. (Ministry's italics.) About 100 ml of water is next added, and the solution titrated immediately with thiosulphate. Following this procedure, it was observed that if there were a delay after mixing the iodide and the sulphuric acid, then iodine was liberated, the amount increasing with time as shown in Table 16, and being particularly rapid in sunlight. Hence, the iodate solution

TABLE 16.—*Iodine Liberated from Strongly Acid Potassium Iodide.*

Time (min.)	ml N/80 Thiosulphate Required
1	2
1	0·1
2	0·19
3	0·28
5	0·48
10	0·8
20	0·96
5 In sunlight	1·1

should be added as quickly as possible after the addition of acid. The order of the addition was subsequently modified, placing water in the bottle first, followed by acid, iodide and iodate, and did not appear subject to any error. Determinations were made in triplicate on all occasions.

(C) Results

(i) *Phenols*

Preliminary experiments were carried out with phenol and the cresols to determine how the permanganate value varied with the period of oxidation. The results are given in Table 17, and are plotted as curves in Figure 15, from which it will be seen that there is initially a very rapid absorption of oxygen. The rate gradually diminishes, but never becomes zero, increasing at about 0·02 g/hr for these compounds at the end of the normal period of the test. The permanganate value at 3 min. is about 72 per cent of that at 4 hr, and at 10 min. it is about 79 per cent of the

TABLE 17.—*Effect of Time on Permanganate Value at 27°C.*

Time (min.)	Grams of Oxygen/Gram of Phenol			
	Phenol	*o*-Cresol	*m*-Cresol	*p*-Cresol
1	2	3	4	5
1	1·19	0·93	0·86	0·78
3	1·40	1·04	1·01	0·97
5	1·42	1·10	1·04	1·02
10	1·50	1·16	1·09	1·08
30	1·59	1·23	1·17	1·14
60	1·68	1·28	1·25	1·21
120	1·78	1·37	1·33	1·30
180	1·85	1·42	1·38	1·35
240	1·87	1·45	1·41	1·37
300	1·88	1·49	1·44	1·41
360	1·91	1·50	1·47	1·44

final amount. Similar values were obtained in the 10-min. test with a few other phenols. From the rapidity of the rise in the first few minutes, it might be better to perform a 10-min. test rather than the present one of 3 min. and to assume that the permanganate value will be about 80 per cent of the 4-hr value.

TABLE 18.—*Influence of Temperature on 10-min. Permanganate Value of Phenol.*

Temperature (°C)	Permanganate Value
1	2
10	1·38
20	1·53
27	1·57
35	1·63
45	1·72
55	1·82
65	1·93

Since the permanganate values of these phenols increase with the period of oxidation at 27°C, it was decided to determine how far an increase in temperature would also influence the degree of oxidation of a phenol. Ten-minute values were determined for phenol at different temperatures, cooling the liquid as rapidly as possible at the end of this time. The results are given in Table 18, where it is apparent that the values increase linearly with the temperature. The values for 20° and 27°C show a certain scatter from the line, whilst that at 27°C does not agree with the value in Table 17. The method of mixing was, however, somewhat different in this experiment and may account for the difference. At temperatures of 27°C and above, the solution became cloudy during the reaction, whilst at 55°C and above solid particles could be observed in the reaction medium.

A further observation resulting from these first experiments was that the 4-hr permanganate value for phenol (1·87) was significantly greater than that at present accepted (1·78). The determination was repeated several times, and gave values always close to 1·87. The greatest difference between the test as conducted at present and that given by the Alkali Inspectors is one of dilution. The experiment was repeated in presence of 220 ml of water instead of 90 ml, but the result was very little different; in fact, it was slightly higher (1·89).

The permanganate values at 27°C for 4 hr for a number of monohydric and dihydric phenols are given in Table 19, in col. 2 of which these values are given in the units in which they are usually quoted, and are compared with values from other sources that are given in col. 3. It will be seen that there can be sometimes a significant disparity between results from different sources. Badger[25] has determined the permanganate values of a number of dihydric phenols. The values are not quoted here, since they have not yet been published in the literature, but some are reasonably close to those in Table 19, whilst a few differ by around 10 per cent. Moreover, the differences do not all lie in the same direction: hence, it must be accepted that there is a possibility of error in the values quoted in Table 19.

Col. 4 in Table 19 gives the amount of oxygen that would be absorbed by 1 gram-molecule of the phenol; and this has then been divided by the atomic weight of oxygen to give the number of atoms of oxygen that have been absorbed by 1 molecule of the phenol (col. 5). The values in this column may then be compared with those in col. 6, which gives the number of atoms of oxygen that would be required to convert the molecule completely to carbon dioxide and water. The experimental value is divided by the theoretical value and the result expressed as a percentage (col. 7).

From these values, it is clear that the simpler molecules absorb more oxygen than the complex ones, in some cases

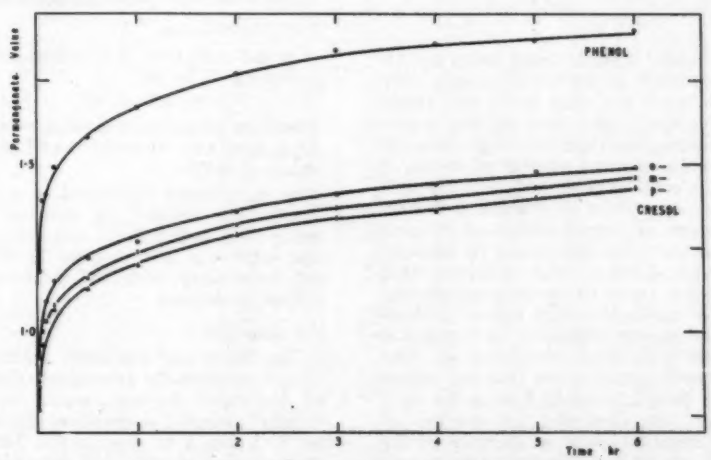


FIGURE 15.—*Permanganate Values of Phenol and the Cresols.*

TABLE 19.—*Permanganate Values of Phenols.*

Compound	Permanganate Value Grams Oxygen/Gram of Phenol		Grams of Oxygen/ Mole of Phenol	Atoms Oxygen Absorbed/ Molecule of Phenol		
	Present Work	Other Sources		Actual	Theoretical	% of Theoretical
1	2	3	4	5	6	7
MONOHYDRIC PHENOLS—						
Phenol	1·87	1·78[1]	176	11·0	14	78·6
o-Cresol	1·45	1·42[2]	157	9·8	17	57·6
m-Cresol	1·41	1·38[2]	152	9·5	17	55·9
p-Cresol	1·37	1·37[2]	148	9·3	17	54·7
2,6–Xylenol	1·13		138	8·6	20	43·0
2,5–Xylenol	1·14		139	8·7	20	43·5
2,4–Xylenol	1·05		128	8·0	20	40·0
2,3–Xylenol	1·19		145	9·1	20	45·5
3,5–Xylenol	1·20		147	9·2	20	46·0
3,4–Xylenol	0·99		121	7·6	20	38·0
2–Ethylphenol	1·27		155	9·7	20	48·5
3–Ethylphenol	1·26		154	9·6	20	48·0
4–Ethylphenol	1·31		160	10·0	20	50·0
3–Methyl, 5–ethylphenol	1·07		146	9·1	23	39·6
3–Methyl, 6–ethylphenol	1·02		139	8·7	23	37·8
2,3,5–Trimethylphenol	0·86		117	7·3	23	31·7
2,4,6–Trimethylphenol	0·89		121	7·6	23	33·0
4–Indanol	1·22		164	10·2	22	46·4
5–Indanol	1·12		150	9·4	22	42·7
1–Naphthol	0·99		143	8·9	23	38·7
2–Naphthol	1·55		224	14·0	23	60·9
DIHYDRIC PHENOLS—						
Catechol	1·34	1·44[3]; 1·35[2]; 1·245[4]	148	9·2	13	70·8
Resorcinol	1·66	1·64[3]; 1·63[2]	183	11·4	13	87·7
Quinol	1·57	1·52[2]	173	10·8	13	83·1
3–Methylcatechol	1·13		140	8·8	16	55·0
4–Methylcatechol	1·12		139	8·7	16	54·4
2–Methylresorcinol	1·30	1·34[2]	161	10·1	16	63·1
4–Methylresorcinol	1·28	1·34[2]	159	9·9	16	61·9
5–Methylresorcinol	1·22	1·34[2]	151	9·5	16	59·4
2–Methylquinol	1·24		154	9·6	16	60·0
3,4–Dimethylcatechol	0·90		124	7·8	19	41·0
3,5–Dimethylcatechol	0·91		126	7·9	19	41·6
3,6–Dimethylcatechol	1·01		140	8·7	19	45·8
4,5–Dimethylcatechol	0·88		122	7·6	19	40·0
2,4–Dimethylresorcinol	0·92		127	7·9	19	41·6
4,5–Dimethylresorcinol	1·03		142	8·9	19	46·8
4,6–Dimethylresorcinol	0·90		124	7·8	19	41·0
2,3–Dimethylquinol	1·06		147	9·2	19	48·4
2,6–Dimethylquinol	0·98		135	8·5	19	44·7
3–Ethylcatechol	0·96		133	8·3	19	43·7
4–Ethylcatechol	1·08		149	9·3	19	48·9
2–Ethylresorcinol	1·18		163	10·2	19	53·7
4–Ethylresorcinol	1·27		176	11·0	19	57·9

References :—
[1] Frankland and Silvester. Ref. 24
[2] Previous investigators for Joint Research Committee.
[3] Linder. Ref. 9.
[4] Badger. Ref. 26.

only a third of the theoretical amount being taken up. It is interesting that the number of atoms of oxygen consumed by a molecule is never less than seven and rarely greater than eleven. Averaging the values for the monohydric phenols, and excluding the relatively high value for 2-naphthol, gives 9·07 as the average number of atoms of oxygen absorbed per 1 molecule of a phenol. For dihydric phenols, the average is 9·14, and for all phenols it is 9·10. The actual number of atoms of oxygen taken up by each molecule is often close to the value that would be required if the molecule were broken down to three molecules each containing two of the carbon atoms of the original benzene ring with the formation of carboxyl groups where $-OH$ or $-H$ is attached, and keto groups where an alkyl group is attached, giving molecules of oxalic or pyruvic acid. This has yet to be proved, but it would mean that the subsequent oxidation of these products would have to be very slow at 27°C. Certainly, the fact that the number of oxygen atoms taken up decreases with an increase in the number of alkyl groups, would indicate that these groups are not oxidized and prevent attack by oxygen.

(ii) *Bases*

Since information was now available on the bases present in ammoniacal liquors[16], it was considered that the permanganate values of the more important ones should be determined, though Linder[9] had shown that the permanganate value of pyridine was nil. Table 20 shows the values obtained experimentally. This indicates that the permanganate values of the pyridines are indeed negligible,

TABLE 20.—*Permanganate Values of Bases.*

Compound	Permanganate Value
1	2
Pyridine	0·01
2–Methylpyridine	0·01
Quinoline	0·40
Aniline	3·70

but that of quinoline is appreciable, whilst that of aniline is substantially greater than any of the phenols. Combining these values with those in Table 9 would result in the contribution of bases to the permanganate value of a coke oven liquor and a vertical retort liquor of between 50 and 100 p.p.m.

(iii) *Thiocyanate*

Frankland and Silvester[24] suggest that the oxidation reaction for the thiocyanate ion is given by the equation

$$CNS' + 3O \rightarrow SO_3'' + CN',$$

which would give a theoretical permanganate value, per 1 g of CNS′ of 0·827, and they obtained this figure experimentally. On the other hand, Badger[26] gives the final oxidation products as CO_2 and $(NH_4)_2SO_4$, which would give the theoretical permanganate value per 1 gram of 1·103, the experimental value then being 75 per cent of the theoretical.

Values have been experimentally determined using both potassium thiocyanate and ammonium thiocyanate. The former gave a permanganate value of 0·82 and the latter 0.828, in excellent agreement with those obtained previously. The amount of thiocyanate in each solution was determined by titration with a 0·1 N silver nitrate solution which had in turn been standardized against a solution of sodium chloride, prepared from the pure dry salt.

(iv) *Thiosulphate*

In the oxidation of thiosulphate, the theoretical reaction is considered to be

$$S_2O_3'' + 2O_2 + H_2O \rightarrow 2\ HSO_4'$$

where the permanganate value would be 1.00 per 1 g S. Both Frankland and Silvester[24] and Linder[9] give an experimental value of 0·856.

In the present investigation, it was found impossible to obtain this value. A number of determinations were made both with sodium and ammonium thiosulphates, and the value was always close to 0·81. The result was still the same when using the greater dilution specified by the Alkali Inspectors.

(v) *Sulphide*

The theoretical oxidation reaction for hydrogen sulphide would result in the formation of sulphuric acid, where 1 g of hydrogen sulphide would require 1·88 g of oxygen. Linder[9] obtained an experimental value of 1·345 for periods of 1, 3 and 4 hr; but in the 3-min. test, where the permanganate concentration was greater, the permanganate value was 1·450.

In the present investigation, the permanganate value of sulphide was determined using ammonium sulphide, an approximately 10-per cent A.R solution being diluted 1 to 1,000 and 10 ml being taken for the determination. The concentration of sulphide was determined by reaction with an excess of standard iodine solution in presence of acid, and titrating the excess with thiosulphate solution. Permanganate values were also determined with a solution of hydrogen sulphide in water. Results were not as repeatable as with the other ions, but fell within the range 1·53 to 1·63 with an average of 1·58 g of oxygen absorbed per 1 g of hydrogen sulphide. This figure is appreciably higher than that of Linder; but it is possible to support his statement that dilution affects the results, since, working under the more dilute conditions of the Alkali Inspectors, a value of 1·42 was obtained. This is still higher than Linder's 4-hr figure, but close to the value he gives for the 3-min. permanganate value.

An interesting observation was made concerning the removal of sulphide from aqueous solution by boiling. The method is suggested in Key's manual[4] as an alternative to treatment with lead carbonate to remove sulphide from liquors prior to determinations of other constituents, though the proportion of liquid that should be distilled is not given.

With a solution of ammonium sulphide at a concentration of about 2 g/1, tests on the distillate indicated that no more sulphide was being distilled over after 20 per cent of the solution had been boiled off. The permanganate value of the residue, however, was still appreciable, being 54 p.p.m. Further distillation reduced the permanganate value to 23 p.p.m. when 30 per cent of the solution had distilled over, but the permanganate value was reduced only to 21 p.p.m. by the time 50 per cent of the solution had been distilled.

(vi) *Summary of the Inorganic Anions*

The experimentally determined permanganate values for the above three inorganic ions are given in Table 21, where they are compared with the values obtained by other workers. Formerly, the determination of thiosulphate has been quoted in terms of S, and that of sulphide in terms of H_2S. In the present investigation, these have been respectively recorded in terms of S_2O_3'' and S", and factors for such ions are also included in Table 21.

TABLE 21.—*Permanganate Values of Inorganic Anions.*

Ion	In terms of :	Permanganate Value		Atoms Oxygen/Ion	
		Previous	Present	Actual	Theoretical
1	2	3	4	5	6
Thiocyanate ..	CNS'	0·827	0·82	3·0	3 or 4
Thiosulphate ..	S	0·856	0·81		
,, ..	S_2O_3''	—	0·46	3·2	4
Sulphide ..	H_2S	1·345	1·58		
,, ..	S"	—	1·68	3·4	4

(D) ASSESSMENT OF THE DIFFERENCE FIGURE

The permanganate values given in Tables 19 and 21 have been employed to determine the extent to which the total permanganate value of a liquor can be accounted for by known constituents. Calculations have been made for most of the same liquors that were used to obtain the bromination factors. As with the bromination results, where a chromatographic band in the analysis of phenols contained more than one phenol, an average permanganate value was used in the calculation. Inorganic ions were determined by the usual methods. From the concentration of a substance in the liquor and the permanganate value per 1 gram, its contribution to the permanganate value of the liquor could be assessed. Results of the calculations are given in Table 22, where the numbers in the first column refer to the same liquors as in Table 13. In col. 10 of Table 22 is the " difference figure " for each liquor, and it will be seen that this is nearly always a positive value, though on two occasions (liquors 22 and 28) the value was negative, and once (liquor 15) zero.

The results in Table 22 have been summarized under the type of plant in Table 23. The averages of the " difference figures " in col. 3 are difficult to assess, since in two of the groups there is only one liquor, and it would seem probable that a lower figure would be obtained for liquors from horizontal retorts if a number of such liquors had

TABLE 22.—*Permanganate Values of Liquors.*

No.	Type of Liquor	Permanganate Value (p.p.m.)								Permanganate Value/g.		
		Monohydric Phenols	Dihydric Phenols	S"	S_2O_3''	CNS'	Total	Experimental Total	Difference	Monohydric Phenols	Dihydric Phenols	Total Phenols
1	2	3	4	5	6	7	8	9	10	11	12	13
1	Coke Oven	3,682	150	—	281	189	4,302	4,900	598	1·68	1·36	1·67
2	,, ...	3,481	268	706	184	369	5,008	6,100	1,092	1·72	1·34	1·69
3	,, ...	1,249	68	—	—	—	—	—	—	1·67	1·36	1·65
4	,, ...	3,243	208	1,394	225	500	5,570	5,650	80	1·72	1·39	1·69
5	,, ...	2,277	267	6,303	110	451	9,408	10,800	1,392	1·65	1·34	1·61
6	,, ...	1,638	508	—	672	1,107	3,925	4,800	875	1·71	1·34	1·60
7	,, ...	2,395	62	648	73	172	3,350	4,400	1,050	1·66	1·24	1·65
8	,, ...	2,591	—	695	81	156	3,523	4,000	477	1·67	—	1·67
9	,, ...	2,022	51	47	162	230	2,512	3,200	688	1·70	1·28	1·69
10	,, ...	2,522	176	134	179	320	3,331	3,900	569	1·70	1·35	1·68
12	,, ... Spent	1,408	—	—	162	271	1,841	2,440	599	1·74	—	1·74
13	Horizontal Retort ..	3,141	501	4,788	400	1,615	10,445	12,000	1,555	1·67	1·25	1·60
14	Intermittent Verticals .. Retort House	8,703	5,991	—	741	640	16,075	16,700	625	1·64	1·33	1·50
15	,, ... Condenser	9,876	1,899	3,696	373	558	16,402	16,400	− 2	1·66	1·31	1·59
16	,, ... Crude	6,713	1,826	2,688	492	615	12,334	12,700	366	1·65	1·30	1·56
17	Low Temperature ..	11,770	5,182	—	700	330	17,980	18,200	220	1·62	1·26	1·49
18	Continuous Verticals .. Crude	7,294	5,963	689	60	2,050	16,056	17,100	1,044	1·62	1·29	1·45
19	,, ... ,,	8,395	4,991	3,881	281	656	18,204	18,800	600	1·60	1·29	1·47
20	,, ... ,,	9,013	2,411	3,480	270	530	15,700	17,400	1,700	1·62	1·22	1·52
21	,, ... Retort House	6,364	13,493	—	400	1,720	21,970	23,000	1,030	1·62	1·31	1·39
22	,, ... ,,	5,991	13,136	—	460	1,915	21,502	21,000	−502	1·61	1·32	1·40
23	,, ... Hot Gas Electro-Detarred	9,844	389	2,268	78	295	12,874	14,000	1,126	1·58	1·25	1·56
24	,, ... ,,	11,673	326	8,568	110	426	21,103	21,800	697	1·60	1·25	1·59
25	,, ... Spent	7,525	2,073	—	92	328	10,018	10,600	582	1·60	1·22	1·50
27	Lurgi .. .. .. Tar Liquor	4,673	653	—	46	74	5,446	6,700	1,254	1·56	1·23	1·51
28	,, ... ,,	6,213	1,572	17	166	123	8,091	7,600	−491	1·53	1·21	1·45
29	,, ... Oil Liquor	7,380	234	958	138	131	8,841	9,800	959	1·59	1·30	1·58
30	,, ... ,,	9,472	673	823	414	189	11,571	11,800	229	1·55	1·25	1·52

TABLE 23.—*Summary of "Difference Figures".*

Type of Liquor	Number in Average	Average "Difference Figure"	"Difference Figure" as Percentage of Total
1	2	3	4
Coke Oven	10	742	16·0
Horizontal Retort ..	1	1,555	13·0
Intermittent Vertical Retort	3	330	3·3
Low Temperature ..	1	220	1·2
Continuous Vertical Retort	8	784	4·8
Lurgi	4	488	6·0
All	28	658	7·4

been analysed. Where there is a number of liquors in an average (coke oven and continuous vertical retorts), the averages are similar at about 750 p.p.m. Hence, the average for all types of liquor (about 660 p.p.m.) may be a significant value. This is shown better in col. 4 of Table 23, where the difference figure is expressed as a percentage of the total permanganate value of a liquor. With coke oven liquors, where the total permanganate value is relatively small, the difference becomes a significant percentage, since it is probable that the accumulation of errors in all the determinations would be less than the 16 per cent for this type of liquor. For most of the other types of liquor, the difference figure is possibly not greater than the total of the errors in all the determinations, since many of these cannot be better than about 5 per cent.

Assuming that the average difference figure of about 660 p.p.m. is significant for all liquors, then it would be due to compounds not accounted for in the analysis. The concentrations of the organic bases in these liquors have not been determined, but it is considered that their contribution would in all cases be in the region of 60 p.p.m., which would then give a difference figure of 600 p.p.m. At present, it is not known what are the types of compounds that have yet to be identified in liquors, and which absorb oxygen from acid permanganate. It is possible that they could be oxidation products, such as those formed from dihydric phenols, but in this case their concentrations would be expected to be least in coke oven liquors where concentrations of dihydric phenols are quite small. If the permanganate value per 1 gram of the unknown material is similar to that of the phenols (i.e., about 1·0), then it is present in solution at a concentration at about 0·6 g/l which is appreciable when compared with concentrations of other compounds.

The presence of chloride is said to increase the permanganate value of an effluent[14], but it has not been possible to relate the difference figure to the chloride concentration in the liquor.

At the present time, therefore, it is not possible to account for the permanganate value difference figure in ammoniacal liquors, but the value is now substantially less than had to be quoted in earlier analyses, where the contribution of dihydric phenols could not be determined.

(E) FACTORS FOR AMMONIACAL LIQUORS

In col. 11, 12 and 13 of Table 22 are the permanganate value factors respectively of total monohydric phenols, total dihydric phenols, and total phenols in terms of oxygen absorbed by 1 gram of the phenol mixture. These factors have been averaged in groups in Table 24. The order of the types of liquor is the same as with the bromination factors (Table 14), except that the permanganate values factors decrease with an increase in the proportion of low-temperature products in the liquor, and this occurs both with monohydric and dihydric phenols.

TABLE 24.—*Permanganate Value Factors for Phenols in Liquors.*

Type of Liquor	Number in Average	Permanganate Value		
		Monohydrics	Dihydrics	Total
1	2	3	4	5
Coke Oven	11	1·69	1·33	1·67
Horizontal Retort	1	1·67	1·25	1·60
Intermittent Vertical Retort	3	1·65	1·31	1·55
Low Temperature	1	1·62	1·26	1·49
Continuous Vertical Retort..	8	1·61	1·26	1·483
Lurgi	4	1·56	1·25	1·51

Where the proportion of dihydric phenols is small, as in the coke oven liquors, the permanganate value factor for total phenols is close to that for monohydric phenols; whereas, the factor for total phenols is substantially lower in the case of vertical retort liquors that contain a relatively high proportion of dihydric phenols. The factor for dihydric phenols in the horizontal retort liquor is apparently not in the correct order in Table 24, and it may be that the analysis was in error; a better value would no doubt have been obtained had more of such liquors been analysed; the factor should possibly be 1·32, giving about 1·65 for total phenols. Table 24 has thus been amended in Table 25 into fewer groups, and these factors are suggested for use in determinations.

TABLE 25.—*Suggested Permanganate Values.*

Type of Liquor	Permanganate Value		
	Monohydric	Dihydric	Total
1	2	3	4
Coke Oven, Horizontal Retort ..	1·69	1·33	1·67
Intermittent Vertical Retort ..	1·65	1·31	1·55
Continuous Vertical Retort, Low Temp.	1·61	1·26	1·49

It is interesting to consider the results obtained when the permanganate value for total monohydric phenols is calculated from their concentration determined by bromination. This involves the product of the bromination factor and the permanganate value factor, which is at present:—

$$0{\cdot}00157 \times 1{\cdot}78 = 0{\cdot}0027946 \quad \text{(i)}$$

For coke oven liquors the values now suggested would give a multiplicand of

$$0{\cdot}0027885 \quad \text{(ii)}$$

and for vertical retort liquors

$$0{\cdot}0027370 \quad \text{(iii)}$$

The ratio of (ii) to (i) is 0·998, and that of (iii) to (i) is 0·979. Hence, for coke oven liquors, there would be no difference between the results for permanganate values calculated by either of the factors (i) or (ii), and for vertical retort liquors only 2 per cent between (i) and (iii). The concentration of monohydric phenols would, of course, be in error using (i).

For most laboratories, only the values for monohydric phenols in Table 25 will be of use at the present time, since the most satisfactory method for determining dihydric phenols or total phenols is beyond general application as it requires the provision of an ultraviolet spectrophotometer, which is a relatively expensive piece of equipment. A simple procedure, although involving the use of such an apparatus, is given in Section VI.

It is possible that a colorimetric method could be developed for the determination of dihydric phenols in liquors, using, for example, the Folin-Denis method for total phenols[27], but this would first require a detailed investigation of the colours and colour intensities produced by all the phenols present in liquors.

VI DETERMINATION OF TOTAL PHENOLS BY ULTRAVIOLET SPECTROSCOPY

(A) Introduction

In a previous Paper presented to The Institution of Gas Engineers[3], a method was described for the determination of total phenols, total monohydric phenols, and, from the difference, total dihydric phenols in ammoniacal liquors by direct measurements of the ultraviolet absorption of the liquor. The discussion of the method in that Paper was incomplete, as the factor to be used in the calculations had not been fully derived and there were differences between experimental results obtained, firstly, from chromatographic analysis, and, secondly, from direct ultraviolet measurements. Some account of later investigations was given in the reply to the discussion on that Paper, but it was considered that an opportunity should be taken to amplify it.

(B) Procedure

The procedure for total phenols in a liquor is first to acidify the liquor and to allow time for sulphur to settle from the solution; then to dilute it sufficiently to obtain an accurate measurement of the optical density at 2,700A (A_1) the best determinations being obtained when the optical density is between about 0·4 and 0·7. At the same time, the optical density is measured at 3,000A (A_2). The acidified liquor is then extracted with four portions of ether, the total volume of ether used being about equal to that of the liquor, and the optical density again measured at 2,700A (A_3) and 3,000A (A_4). The difference between the two optical densities measured at 2,700A is proportional to the concentration of phenols in the liquor, but the value has to be corrected by subtraction of the difference at 3,000A. The correction is necessary since, whereas phenols that are at present in ammoniacal liquors should have almost negligible optical density at 3,000A, the difference A_3-A_4 is an appreciable amount. This partly results from dilution of the extracted liquor by the ether that it dissolves and partly from substances other than phenols that are removed in the extraction and which have measurable optical densities at the higher wavelength. The total concentration of phenols in g/1. in the liquor (c) is given by:—

$$c = f.d.a\ (A_1 - A_2 - A_3 + A_4) \quad \ldots \text{(i)}$$

where f is a factor,

d the number of times the liquor was diluted,

and a the ratio of the volumes of liquor after and before acidification.

Total monohydric phenols may be obtained in the same way from a steam distillate of the liquor produced under conditions specified in Section III(E). Here the ether extraction may be omitted since the value at 3,000A is negligible even before extraction and the optical density is very small at 2,700A after ether extraction.

(C) Calculation of the Factor

The factor (f) required in equation (i) above has been calculated in a similar manner to those for bromination and permanganate values, employing the chromatographic analysis of the same series of liquors and the extinction coefficients for pure phenols in aqueous solution. The latter values were given in Table 9 of the previous *Research Communication*[3] and need not be included again here. Results of the calculations are given in Table 26. Col. 3 contains the factors for total phenols calculated directly in the way described; those in col. 4 were determined from the ultraviolet spectrum of the liquor as described in sub-section (B) using equation (i) and taking the total concentration of phenols from the chromatographic analysis. There are differences between corresponding values in these two columns, but these are reduced on averaging. Col. 5 contains the factors for total monohydric phenols. The values for dihydric phenols in col. 6 show a greater degree of scatter, but these are not required in determinations, since dihydric phenols are best determined by difference between total and monohydric phenols.

Average values for the different types of liquors, grouped in the same way as in Tables 14 and 24, are given in Table 27. Again, the same order of values is obtained; differences are probably not so great as they appear in Table 27, since it is likely that only the first two digits

TABLE 26.—*Factors Calculated for Ultraviolet Determination of Phenols in Liquors.*

No.	Type of Liquor		Total Phenols		Monohydric Phenols	Dihydric Phenols
			From Individual Phenols	From Spectrum of Liquor		
1	2		3	4	5	6
1	Coke Oven		0·0686	0·0648	0·0681	0·0795
2	,, ...		0·0678	0·0658	0·0668	0·0795
3	,, ...		0·0684	0·0657	0·0684	0·0685
4	,, ...		0·0672	0·0638	0·0669	0·0702
5	,, ...		0·0698	0·0703	0·0688	0·0766
6	,, ...		0·0694	0·0693	0·0672	0·0755
7	,, ...		0·0689	0·0694	0·0686	0·0781
8	,, ...		0·0683	0·0675	0·0683	—
9	,, ...		0·0678	0·0628	0·0675	0·0784
10	,, ...		0·0682	0·0639	0·0672	0·0785
11	,, ...		0·0696	0·0728	0·0680	0·0816
13	Horizontal Retort		0·0702	0·0716	0·0682	0·0820
14	Intermittent Vertical Retort	Retort House	0·0716	0·0739	0·0694	0·0744
15	,, ...	Condenser	0·0700	0·0684	0·0684	0·0758
16	,, ...	Crude	0·0704	0·0716	0·0686	0·0760
17	Low Temperature		0·0718	0·0697	0·0700	0·0751
18	Continuous Vertical Retort	Crude	0·0723	0·0745	0·0698	0·0749
19	,, ...	,,	0·0711	0·0700	0·0701	0·0733
20	,, ...	,,	0·0720	0·0680	0·0694	0·0805
21	,, ...	Retort House	0·0711	0·0714	0·0701	0·0715
22	,, ...	,,	0·0706	0·0717	0·0704	0·0707
23	,, ...	Hot Gas Electro-Detarred	0·0709	0·0696	0·0708	0·0728
24	,, ...	,,	0·0700	0·0648	0·0701	0·0674
25	,, ...	Spent	0·0722	0·0698	0·0706	0·0772
27	Lurgi	Tar Liquor	0·0723	—	0·0718	0·0751
28	,, ...	,,	0·0738	0·0722	0·0728	0·0772
29	,, ...	Oil Liquor	0·0706	—	0·0705	0·0738
30	,, ...	,,	0·0726	0·0700	0·0722	0·0765

TABLE 27.—*Average Factors for Ultraviolet Determinations.*

Type of Liquor	Number in Average	Total Phenols		Monohydric Phenols	Dihydric Phenols
		From Individual Phenols	From Spectrum of Liquor		
1	2	3	4	5	6
Coke Oven	11	0·0685	0·0669	0·0678	0·0766
Horizontal Retort ..	1	0·0702	0·0716	0·0682	0·0820
Intermittent Verticals	3	0·0707	0·0713	0·0688	0·0754
Low Temperature ..	1	0·0718	0·0697	0·0700	0·0751
Continuous Verticals	8	0·0713	0·0700	0·0702	0·0735
Lurgi	4	0·0723	0·0711	0·0718	0·0757

are significant. The horizontal retort liquor does not correspond closely with the coke oven liquors with respect to total phenols, but the agreement is better for monohydric phenols.

Taking the values to two significant figures, it is suggested that a value of $f = 0{\cdot}069$ be used in equation (i) for the determination of total phenols in coke oven liquors and horizontal retort liquors, and $f = 0{\cdot}071$ for all other types. Similarly, for monohydric phenols, the respective factors should be $f = 0{\cdot}068$ and $f = 0{\cdot}070$.

VII CONCLUSIONS

In considering some of the procedures used in the analysis of ammoniacal liquors, it has been found that certain improvements were necessary to reduce errors in the determinations. Whilst no profound alterations in the methods have been required, some changes in analytical details have been suggested, and factors used in the calculations have been adjusted in consequence of the more detailed analyses that were possible by chromatography.

Thus, in the determination of total monohydric phenols, the separation of these compounds from the dihydric phenols, and from other constituents of the liquor that would interfere in the determination, is normally made by distillation of the aqueous solution. The separation depends upon the monohydric phenols being the only compounds that are steam-volatile under the conditions of the distillation. A detailed investigation of the steam volatilities of the phenols has shown that the conditions at present employed will, in fact, give the desired separation, but that a definite minimum proportion of solution must be distilled to lead to a quantitative recovery of monohydric phenols.

Experiments have indicated that phenol is one of the least steam-volatile of the monohydric phenols; whilst, amongst the dihydric phenols, the catechols are appreciably volatile in steam. It is interesting to discover that oxidation products of catechols are also steam-volatile, and that both they and the catechols are prevented from distilling by the presence of lead carbonate. A significant fact is that a number of monohydric phenols can be distilled from solution in presence of a strong alkali; and, in the case of 2, 6-xylenol, 50 per cent of the compound will be lost from solution if 90 per cent of the solution is distilled off. This latter observation has an important bearing on the preliminary treatment of the sample, where bases are removed by concentration of an alkaline solution of the liquor to a relatively small volume. It has thus been suggested that this procedure would be best omitted, and the separation of bases be obtained at a later stage by distillation of the monohydric phenols from acid solution.

The determination of monohydric phenols is dependent upon the amount of bromine that these compounds absorb from a standard bromate—bromide solution. It has always been appreciated that different phenols absorb different amounts of bromine, and, since it has not been possible in the past to determine the proportions of the different phenols that are present in a liquor, the result had to be returned as phenol (C_6H_5OH). Although the literature on liquor analysis has indicated that a compound such as *o*-cresol could take up only 2 atoms of bromine instead of the 3 atoms taken up by phenol, there appears to be no recognition that, in presence of excess bromine, it absorbs substantially more bromine than this, and the number of atoms is not an integral amount. The phenomenon has, however, been known for some time. In the present investigation, the bromination values for a number of phenols have been determined, and, in conjunction with results of the chromatographic analysis, it has been possible to suggest a different factor from that used at present in the calculations, to give a more realistic figure for total phenols, which does not have to be quoted in terms of phenol. The test must always be conducted under the same conditions to give the correct result, and the details are somewhat different from those at present used in liquor analysis.[4]

An additional method is given in this *Research Communication GC*70 for the determination of total monohydric phenols and depends upon the measurement of the ultraviolet absorption of the steam distillate. The method is suitable for the same range of phenol concentrations as the bromination procedure. Its chief advantage is that it is independent of compound formation, and the determination involves only one measurement on the original solution that has been suitably diluted. The sole disadvantage, but which makes it unsuitable for use in most laboratories, is the expense of the spectrophotometer that is required. Factors have been calculated suitable for determinations with ammoniacal liquors.

The determination could also be made colorimetrically, using 4-aminoantipyrene. The procedure has not been investigated here, since it is considered that the bromination technique will suffice for all ammoniacal liquors that may be encountered, the lower limit of its range being below that which would ever be required in liquor analysis. Should it become necessary to determine concentrations below about 20 p.p.m., then in using 4-aminoantipyrene the relative colour intensities of the phenols would have to be combined with their measured individual concentrations to give factors that could be used in subsequent determinations. Some phenols (e.g., *p*-cresol) produce very low colour intensities with this reagent, and their presence could thus introduce a significant error into an analysis.

The least satisfactory feature of liquor analysis is the determination of dihydric phenols. This can be readily achieved by measurement of the ultraviolet absorption of the liquor to give total phenols. As mentioned above, the cost of the instrument in most cases precludes its use. Total phenols may be determined colorimetrically with the Folin-Denis reagent. The method would also require a factor to be derived for the calculation, and this has not yet been obtained. It is probable that the phenols would have first to be separated from other constituents in the liquor. This might be done by solvent extraction of the acidified liquor, which should remove only the phenols (ignoring small amounts of neutral organic compounds), and it should then be possible to make the determination colorimetrically. If the solvent and the monohydric phenols

could be removed from the extract (e.g., by steam distillation in presence of lead carbonate), then the dihydric phenols should remain behind and, after acidification, they could be determined by their permanganate value. It has been observed, however, that, in presence of lead salts, dihydric phenols appear to be susceptible to aerial oxidation, and this would prevent their proper estimation. If it were possible to remove the solvent alone, then the total permanganate value could be determined, and the value for monohydric phenols subtracted from it. A solvent that had no permanganate value would be the best to employ. These are all points that might be investigated.

In this *Research Communication GC*70, permanganate values of most of the constituents of liquors have been determined, and some of the values for relatively important constituents do not agree with the previous determinations. The most serious disagreement for constituents that are often present in substantial proportions occurs with sulphide, thiosulphate, and phenol. It has not always been possible to decide where the error lies, and it has been necessary to accept those of the present investigation in subsequent calculations. No suggestions are made for changes in the analytical procedure, since the test is somewhat arbitrary, and details have become standardized over the years. Results have been employed to determine the permanganate value "difference figure" which is given by constituents not yet identified in liquors and by errors in all the determinations. Formerly, the difference figure had always contained the contribution of dihydric phenols, but it has now been possible to account for these compounds. With the liquors that have been analysed, the average value for the difference figure was 600 p.p.m., there being some negative results and a scatter from −500 p.p.m. to +1700 p.p.m. The positive values, of course, predominate to give the average. The figure could be significant for coke oven liquors, but it is considered possibly to be within the limits of experimental error for other liquors.

In any future investigations on the analytical methods used for ammoniacal liquors, determinations of dihydric phenols and those of some of the inorganic ions should be considered further. Determinations of ammonia and the Aldridge method for CNS′ are satisfactory, whilst an electrometric titration procedure has been developed for the determination of chloride[28]. The present methods for determinations of sulphide and thiosulphate are not entirely satisfactory, and improvements would be desirable.

Acknowledgments

The Authors wish to express their thanks to a former colleague, Mr. J. C. Crowther, who began the assessment of the analytical procedures and made most of the determinations of inorganic ions in the liquors.

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PRESENTATION, DISCUSSION AND REPLY

Presentation

Dr. L. Barker presented the paper and summarized its contents.

Discussion

Mr. E. H. M. Badger (London):—Those who are concerned with the disposal of gas liquor have been much indebted to the investigations, on the composition of liquors, that have been carried out at the University of Leeds over the past 10 years. This paper is the third of a series, the first of which described work initiated by Dr. W. H. Blackburn on the extraction of the phenols with a solvent, and their identification by fractional distillation. The second paper was given, two years ago, by the present authors, on the determination of the phenols by means of chromatography. This paper deals with the analysis of liquors, using simpler methods than those employed in the two previous investigations.

The first third of the paper describes the behaviour of various phenols on distillation from aqueous solutions, which is a preliminary step in the standard determination by the bromate method, and I have little comment to make except to express my appreciation of the large number of useful data

presented. The effect of lead on preventing the volatilization of catechol may not have been specifically stated before, but would be expected to follow from the observation, noted in the Alkali Inspector's 64th Annual Report, that lead salts precipitate catechol from solution. It was for this reason that it was suggested in the 65th Report that the use of lead carbonate for the removal of sulphide prior to the determination of the permanganate value of crude liquors should be discontinued. The substitution of zinc sulphate for lead carbonate avoids this loss of catechol and is now the standard procedure in the permanganate test.

The Authors' work leads to suggestions for modifications in the preliminary steps in the bromate method for the determination of monohydric phenols, although it may be noted that when bases are present the evaporation with alkali was to be replaced by a second distillation, so there may not be much saving in time. These modifications appear to be sound, but I am less happy about the suggestion that the bromination stage should be extended to 30 to 60 min in the presence of excess bromine.

I feel that it is intrinsically better to use a method that leads to the production of definite chemical end-products, as occurs when the bromine is not in excess, than to use one that produces very indefinite end-products. The criticisms of the accuracy of the present methods of bromination do not seem to me to be very well founded. The errors due to the burette readings, which, incidentally, are not doubled when there are four readings instead of two, must surely be related to the net amount of bromine used up, and it does not really matter if the back titration is large or small. Losses of bromine vapour can be made insignificant by keeping the bottle stoppered, except for the few seconds during which the bromate solution is being added. The real test of this method lies in the precision of the experimental results obtained and, in his letter to *Industrial and Engineering Chemistry* (reference 19 in the paper), A. W. Francis quoted results for individual cresols and mixtures which were within ½ per cent of the theoretical values. My own experience with known amounts of phenol and cresols confirms that high accuracy can be obtained by the present standard method of bromination.

The Authors state that bromination must be carried out under rigorously standardized conditions; one would expect that the composition of the mixture of compounds formed by the overbromination method would be sensitive to temperature. There is no indication of the reproducibility of replicate determinations of individual phenols, or of the mixtures in liquors, and it would have been better if we could have repeat determination by both methods of bromination in order to assess their relative accuracy. Mention is made of "re-blueing" after the final titration with thiosulphate; this is more likely to happen when some of the bromine is rather loosely held after overbromination. It is always rather disconcerting when there is a very rapid re-blueing. One does not quite know whether to stop at the first disappearance of colour or to go on titrating until the solution is stable for a reasonable period.

A possible advantage of the overbromination method is one that Dr. Barker brought out in his presentation. This is that the weight of bromine absorbed per gram of *o*-cresol is much nearer to that of phenol than in the standard method, and, therefore, variations from liquor to liquor in the ratio of *o*-cresol to phenol would not give rise to much inaccuracy when a constant factor is applied. There would, however, be inaccuracies due to changing proportions of the other phenols. Thus, relative to phenol, *p*-cresol only takes up 70 per cent as much bromine and 2,4-xylenol about 55 per cent.

Some mention is made in the paper of colorimetric determinations of phenols. Undoubtedly, the quickest method of determining monohydric phenols is to apply the amino-antipyrene test to undistilled samples of sulphide-free liquor. This reagent gives no colour with catechol, but reacts slightly with resorcinol, and this balances to some extent the relatively weak colour formed with *p*-cresol. When the reagent is calibrated against pure phenol, multiplication by a factor of 1·15 of the results obtained with mixed phenols in liquor usually gives values in good agreement with those obtained by chromatography.

The Authors state that they have not made measurements of the colours produced by individual phenols with the Folin-Denis reagent. We have done this for 22 different phenols at Fulham Laboratory, but I shall not quote the results now. Resorcinol, catechol and three of the substituted catechols give higher colour intensities per unit weight than does phenol, and, in general, the determination of total phenols by this method gives a result about 10 per cent higher than by chromatography.

I have not much to say about the section on the permanganate values of phenols, except to confirm that our own results are in reasonable agreement with those of the Authors. I think, however, that reference should have been made to the values given by Mr. P. Wedgwood, in 1951, in a paper to the London and Southern Section of The Institution of Gas Engineers.

Finally, I should like to say a few words about organic compounds other than phenols, which are present in gas liquors. In an endeavour to determine the nature of the residual compounds left in the liquor after biological oxidation, we have extracted the liquor with ether under various conditions, in order to classify the compounds into phenols, acids, bases, neutral oils, *etc.* Determinations of carbon were made by the wet method on each fraction, and the results expressed as a percentage of the total carbon in the liquor. About 6 per cent of the total carbon was contained in compounds that could not be extracted. The amount in the so-called "humic acid" fraction was only 0·4 per cent. On one occasion, the amount of humic acids appeared to increase after partial biological treatment, but it diminished again after further treatment. Our present evidence is that humic acids do not form a very significant proportion of the residual compounds. When the same extraction technique is applied to biologically treated liquors, some compounds are obtained in each fraction, but it is clear that their nature has changed. This is shown by working out the ratio of permanganate value to carbon content for each fraction. Thus, for the phenol fraction, the ratio is about 1·8 in the untreated liquor, which is in agreement with the figure expected from determinations of the permanganate value of individual phenols, as made by the Authors and ourselves, and their known carbon content, but, after biological oxidation, the ratio can be as low as 0·43. This suggests the presence of highly oxidized compounds that can no longer be true phenols. The overall reduction in permanganate value, taking the liquor as a whole, is always greater than the overall reduction in total carbon. After biological treatment, the proportion of compounds that cannot be extracted with ether becomes relatively more important.

We have recently acquired, at Fulham Laboratory, an electrophoresis apparatus for the determination of organic acids. This method will be applied to liquors before and after biological oxidation and should help to identify some of the compounds that are still unknown, but the complete identification of the compounds that can be found in gas liquors is a problem that will tax the resources of all workers in this field. We look forward to several more papers in the series by Dr. Barker and Mr. Hollingworth.

Mr. G. W. Cherry (Birmingham):—This is a "down-to-earth" paper of everyday use and not the highly academic kind sometimes presented, although the latter are necessary for the pursuit of knowledge so essential to science.

The paper falls into three main sections, and I should like to deal with each section separately.

Determination of Phenols—both monohydric and polyhydric: This is most useful. The determination of these factors for the various types of liquor saves a routine analytical laboratory a lot of work.

For the determination of monohydric phenol, the West Midlands Gas Board has hitherto followed in principle the method quoted by Key. Warnings have come from various sources from time to time, however, about the distillation and bromination peculiarities of phenols, and at Birmingham we have done a little work on the determination of pure phenol by this method. As a result of this work, whereas Key, after removal of hydrogen sulphide evaporation with caustic soda, *etc.*, says "distil over 250 cc into a 500 cc flask and make up to the mark", we have washed into the litre flask so that the volume

is not more than 500 cc, and then have distilled not less than 300 cc into a 500 flask and made up to the mark, without adding any water during the distillation. From Table 5, it would appear that we have been getting at least 96 per cent of monohydric phenol over. Our final determination is always carried out by excess bromination and back titration with $Na_2S_2O_3$. The loss of phenols in alkaline solutions is surprising.

The investigation into the distillation of catechols and oxidized catechols is interesting. I have often thought how like cookery the distillation of monohydric phenols is—at last we have the real reason for the "pinch" of $PbCO_3$, and the "salt to taste", and I can now satisfy my juniors' questions with more conviction than hitherto.

The distillation procedure given on pp. 233 and 234 of the paper is just what is wanted, and I have put it into effect already. We have often been warned about the variations in the bromination of the many monohydric phenols, and the new factors determined are again of great value to a routine laboratory that has not time to do it itself. The different number of bromine atoms used by the various phenols has been realized, but it needed the work, together with the time and apparatus, described in this paper to resolve the difficulties. The best we have been able to do hitherto was to report as equivalent phenol, C_6H_5OH.

I know that Mr. E. H. M. Badger now recommends that monohydric phenols should be determined colorimetrically by 4-amino-phenazone, total phenols colorimetrically by Folin-Denis reagent, and polyhydric phenols by difference, and he has shown that the various interferences and abnormalities in colour intensities by chance almost cancel each other out, and should, theoretically, therefore, give approximately correct results. We have found, however, that with the continuous vertical retort liquors we have to deal with in the West Midlands the dilution necessary is up to 5,000 times, and then experimental error, inaccuracies in apparatus, *etc.*, make these colorimetric methods very unreliable for routine purposes, using junior staff. We find that the distillation and bromination method gives the most reliable results for our particular liquors.

Permanganate Value: The Authors state that the merits of the method have not been considered, but they then continue to show how empirical a method it is and how far short of completion it carries oxidation. The factors determined for phenols, *etc.*, are certainly very useful, but it is noteworthy that the average "difference" figure quoted (660 p.p.m.) is admitted to be of the order of the possible experimental error.

I would suggest that the permanganate value does not give a very realistic figure and that it should be abandoned in favour of a better oxygen-absorption method. I have in mind the dichromate value. We in the West Midlands have done a considerable number of dichromate value determinations on gas liquors, and can produce figures that indicate that *complete* oxidation occurs—except for nitrogen compounds and those yielding nitrogen gas.

Further, we can produce figures that indicate that the dichromate value plus correction for nitrogen (determined in the SCN′ and NH_3 analyses) gives an ultimate oxygen demand in very close agreement—in many cases identical—with the ultimate oxygen demand calculated from the CNS and H contents of the liquor. In fact, we often calculate the ultimate oxygen content of a liquor as dichromate value plus 3·75 times ammonia content.

There would be great resistance to the change from permanganate value to dichromate value.

An investigation into the merits of the dichromate value might be a very useful future course for research at Leeds, and I should like Dr. Blackburn and his colleagues seriously to consider it.

Returning to permanganate value, the error mentioned in the standardization of N/80 thiosulphate might be expected—

$KI + H_2SO_4 = HI$ atmospheric oxidation I_2 on standing.

The 10 min test = 80 per cent × 4 min permanganate value seems a good suggestion since an *accurate* 3 min test is difficult in practice. The permanganate value/time curves are steep at three min, and a few seconds can make an appreciable error.

The difference figure of 660 p.p.m. unaccounted for, if significant, could possibly be due to neutral unsaturated compounds—ethylenic or acetylenic oils from tar. The Authors say that in this work it was arranged that 10 to 15 ml of permanganate was used. We have always worked it so that as near to, and not more than, 50 per cent permanganate is used up. We can confirm that chloride increases permanganate value, but not if 25 per cent phosphoric acid replaces sulphuric acid in the test.

Determination of Total Phenols by Ultraviolet Spectroscopy: I am not fully qualified to comment here, since we have only just acquired an ultraviolet spectrophotometer, and are still learning how to use it. We have some experience in the paper chromatographic separations of phenols in liquor. The factors determined in this section are again of great use.

There is no mention of the Bunte method for the determination of higher tar acids. Could we have an official recommendation that this be abandoned? I am sure that the method discloses nothing at all, but some engineers still ask for the figure.

The Aldridge colorimetric method for SCN′ is mentioned. I understood that this method was not now favoured, since it used benzidine, a proved carcinogenic substance.

We now use the pyridine-pyrazolone method, which gives very satisfactory results.

We find Key's H_2S and S_2O_3'' methods adequate for our purpose, but it is agreed that they could, with advantage, be improved.

To sum up, the information given in this paper on the determination of phenols is of great value, but I suggest that the work described on the permanganate values indicates that this method should be abandoned in favour of a method that gives a more realistic value for oxygen absorption. I suggest also that the dichromate value should be seriously considered.

Dr. A. C. Monkhouse, C.B.E. (London):—As I have been connected with this work from the very beginning, I would like to express great appreciation of the progress made by Dr. Blackburn and his staff, as indicated by the paper by Dr. Barker and Mr. Hollingworth. When we started, we had a great advantage, in so far as Mr. Linder, who is the Assistant to the Chief Alkali Inspector, had worked on a number of methods; we therefore had something to go on. We did know a little why we did these things, but one had to be very careful, and I agree the phenol method, particularly where we used a dihydric phenol method, was one that required a little care. We knew nothing then about the composition of monohydric phenols and, in particular, of the polyhydric phenols. We rather assumed it was mainly catechol, and adopted a method of oxygen absorption. We did get some measure of success, because, presumably, the darkening of the liquor was rather important. So much progress has been made since then.

I would like again to pay tribute to the work of Mr. Linder in the beginning, and I should like to say how much I appreciate the progress that has been made by chromatography and by ultraviolet spectroscopy. The progress has been great and we know so very much more. There are so many things in ammoniacal liquor that I am afraid it will take a long time before we discover all of them.

Written Contribution

Mr. N. R. Hall (Kettering), wrote:—I would like to comment on the influence of cyanide on the bromate method for phenols. I feel that the conversion to thiocyanate by means of ammonium polysulphide is unnecessary, on theoretical and practical grounds. First of all, the concentration of cyanide normally encountered in carbonization liquors is low in relation to the phenol concentration; secondly, if the cyanide is allowed to distil over with the monohydric phenols and the bromate procedure is applied, any cyanide forms cyanogen bromide, which, when KI is added to liberate iodine by reaction with the excess bromine, also reacts with the KI to liberate a quantity of iodine equivalent to the amount of bromine used to form CNBr. The net result of this is that cyanide does not interfere and the bromine consumption is

entirely due to the phenols. The equations for the reactions are as follows:—

(i) *Bromination:*

$$HCN + Br_2 = CNBr + HBr$$

(ii) *Addition of* KI

$$CNBr + 2KI = KCN + KBr + I_2$$

I have actually tried this out by adding various amounts of KCN solution to a measured volume of standard bromate-bromide solution, making acid with HCl, allowing to stand, for several minutes, then adding KI, again allowing to stand, and then titrating with standard thiosulphate. No interference in the relationship between the bromate-bromide solution and the thiosulphate occurred as a result of the presence of the cyanide.

Written Reply

The **Authors,** in reply, wrote:—We first desire to thank the contributors to the discussion for their amplification of points mentioned only briefly in the paper.

The section of the paper dealing with the steam distillation of phenols is mainly one of tabulated results and has, therefore, not produced much comment. With respect to preventing the distillation of catechols in steam, although one might predict that catechol would not distil from a solution containing lead carbonate, there could not be an absolute certainty that its homologues would be completely held back; for, since the proximity of alkyl groups can so reduce the acidity of the hydroxyl group in monohydric phenols that distillation from alkaline solution is not prevented, it might be expected that lead salts of catechol homologues would also be subject to hydrolysis. Certainly, one could not predict what would be the effect of lead carbonate on oxidized catechols that would be formed during the evaporation of an alkaline solution of a liquor for prior removal of bases.

Determination of monohydric phenols by bromination has obviously caused more discussion, and here it would seem that the main controversy is one between the use either of a slight excess of bromine, obtained by titration, or of an appreciable excess where the bromine is allowed to react for a longer period of time. Accepting that the first procedure appears to give products in which a definite number of bromine atoms is combined with one molecule of a phenol, the overbromination that occurs in the second procedure attains a reasonably steady state in the period suggested for the reaction even though the number of bromine atoms is rarely an integer. The main point, surely, is that both methods are in use at the present time, and, depending on which authority one follows, different results will be obtained. Obviously, either one or the other of the methods being taken must be used by all concerned with liquor analysis for there to be agreement between results from different sources. The Authors are not really worried which procedure is chosen; the original reason for the one they have considered in detail in the paper was that it was inherited from their predecessors. It did seem, however, that the elimination of the first titration with the bromate-bromide solution resulted in a simpler procedure, particularly since it appeared difficult to judge the "end-point", which is supposed to involve only a small excess of bromine.

It is interesting to find that the presence of cyanide does not affect the determination of phenols by bromination. The conversion of cyanide to thiocyanate in presence of ammonium polysulphide was apparently introduced by Skirrow[10] to eliminate interference in the determination of phenols by the absorption of iodine. He stated that the presence of cyanide "caused too large an amount of iodine to be taken up", the reaction of iodine with phenols being conducted at 60°C and in sodium hydroxide solution. With bromination, however, the reaction of cyanide with iodine does not occur since it is carried out at room temperature in acid solution.

The reproducibility of bromination results was not given in the paper, but in most instances the difference of duplicate determinations was very small, being about 0·05 ml. In a few cases, the difference was about 0·1 ml, though where re-blueing occurred, it was sometimes difficult to judge the end-point, and differences around 0·2 ml were obtained.

The Authors cannot see why the accumulative error in taking a number of burette readings should not be proportional to the number of readings, but it must be admitted that the volume of the back titration does not affect the accuracy. However, compared with the other inaccuracies that can arise in the procedure, the error resulting from estimating a burette reading is relatively unimportant.

Although colorimetric procedures for the determination of phenols in liquors have not been considered in the paper, they have appeared in the course of the discussion. Here, again, the Authors have no detailed experience of these procedures. Assuming that the technique of bromination is satisfactory, then it will hardly ever be necessary to use colorimetric methods for monohydric phenol determinations in liquors, since bromination should cover all concentrations that will be encountered.

The least satisfactory feature of liquor analysis at present is that there is no really good method for the determination of dihydric phenols in routine analysis. Ultraviolet spectrophotometry is no doubt the best method, but, for most laboratories, the colorimetric determination of total phenols by the Folin-Denis reagent would possibly be more convenient to adopt. We are certain that anyone who has experience of the analysis of dihydric phenols would agree that the Bunte burette aeration test is unsatisfactory, since it gives a result that cannot be quoted in terms of concentration, and will not include resorcinols in the determination. It should, indeed, be officially replaced by some other procedure.

Consideration of the permanganate value test is also mainly concerned with whether this method should be discarded, this time in favour of the dichromate value. Again, we must agree that the permanganate method is not very satisfactory, since the oxidation rarely proceeds to completion, whereas dichromate oxidation usually does. Probably, the main disadvantage of the dichromate method results from the presence of chloride in the sample, errors being introduced by variability in the oxidation of the chloride ion to chlorine and from oxidation by the chlorine of nitrogen compounds to nitrogen. Thus, 4 p.p.m. of chloride is approximately equal to 1 p.p.m. of dichromate value, and in most liquors chloride is present at concentrations greater than 1,000 p.p.m. Apart from this, we can see no reason why the permanganate test should not be replaced by the dichromate method, since the chloride difficulty is surely not unsurmountable. So far, the method has not been investigated at Leeds, but it would seem that it is time that the relative merits were assessed for liquor analysis.

On the other hand, since the Authors have been mainly engaged in the determinations of individual constituents of liquors, the extent to which a solution may be oxidized by a chemical reagent has always seemed rather unsatisfactory as a method of chemical analysis. Thus, it can give no indication whether the material responsible for the permanganate value is organic or inorganic, nor can it yield even an approximate figure for the concentration of unknown polluting material, and one is, therefore, compelled to supplement the test with other determinations. Even when used solely as a means of estimating the extent to which the material can cause pollution, one has still to find out what are the substances present, for polluting characteristics would be different according to whether the permanganate value were due to the presence of, say, thiocyanate or thiosulphate, whereas a high concentration of cyanide might be present, yet it would not have a permanganate value.

We are glad that the permanganate value results of Mr. Wedgwood have been mentioned. These were first brought to our notice by Dr. R. L. Cooper after the paper had gone to the publishers, and it would seem that the results are in good agreement with those published here. In this respect, it is interesting to observe how little notice can at times be taken of published results, for this publication appeared in 1951 and contains a permanganate value for phenol slightly higher than the one we obtained, and yet there has never been an amendment of the value in use, though this is some 5 per cent lower. One therefore sometimes wonders if accurate analysis of ammonical liquors is of much interest to those who produce them, since, apart from recovery of ammonia, the material is of no further use to the gas industry. It would be interesting to make a survey of the analysis undertaken in various laboratories to find out what methods are actually in use.

AN INVESTIGATION OF TUNNEL BURNER NOISE

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The Joint Research Committee of The Gas Council and The University of Leeds

RESEARCH COMMUNICATION GC74

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I SUMMARY

A review of the literature on the mechanism of noise production in combustion systems indicates that, in the case of tunnel burners, the oscillations are governed by the Rayleigh criterion, coupled with the possibility of standing waves in the mixture supply pipework.

In order to investigate this hypothesis, a series of simplified single-port tunnel burners was constructed. The results obtained confirm the postulated mechanism and indicate that the upstream conditions exert a dominant effect on the generation of organ-pipe oscillations.

The perforated-back plate type of tunnel burner was chosen for full-scale investigation since it is notoriously prone to noisy combustion. The effects of varying several parameters are presented in the form of combustion-stability diagrams, which clearly indicate the influence on noise production of tunnel length and back plate thickness.

Only preliminary results are presented in this Paper, but some indications are given as to the future lines of research.

II INTRODUCTION

In a previous Paper[1], the growing importance to the Gas Industry of the use of high-velocity tunnel burners was indicated, and it was pointed out that a serious disadvantage of this type of burner is that it sometimes gives rise to a highly unpleasant noise. A survey of relevant literature on the mechanism of noise production was presented, together with a summary of previous work on noise suppression.

The problem of combustion noise is by no means confined to the Gas Industry, since there is a possibility of oscillations being produced whenever a flame is burned in a duct or a confined space. One example is the "rough burning" or "screech" of rocket motors, in which the oscillations may reach such a high amplitude that the combustion chamber disintegrates. Although much of the work on combustion instability in rocket motors is not directly applicable to gas burners, a selection of some of the theories evolved, which appear to be relevant, has been included in Section IV.

It is quite possible that several modes of oscillation may occur in a practical tunnel burner, but in this preliminary

investigation attention has been focused on the organ-pipe type. In order to assist in the understanding of unfamiliar terminology and concepts, it was considered desirable to include a short account of the theory of standing waves in tubes. (Section III.) While the ultimate objective of the work is obviously to provide sufficient data to enable quiet burners to be designed, some simplification is essential in the apparatus used to investigate the fundamental mechanism. The experiments described in Section V were performed on an idealized combustion system of this type and the results need not necessarily apply *in toto* to a full-scale industrial tunnel burner, because several complicating factors are introduced by a practical injection and manifold system.

Since this research programme is primarily concerned with combustion noise, the multiport or perforated-backplate type was chosen as a full-scale burner. Francis[19] has stated that, in general, this type of burner is more liable to give combustion instability than those with single ports. Although each type of burner has its adherents, it is not the Authors' intention to assess their relative merits.

In view of the large number of possibly interdependent variables involved, it must be emphasized that the investigation is by no means complete. It was decided, however, to publish the results already obtained in the form of this interim report, since they may be of some interest to those concerned with burner design.

List of Symbols

A (in.)	Radius of tunnel.
a (in.)	Radius of mixture tube.
c (in./sec)	Velocity of sound.
e (in.)	End-correction of standing-wave tube.
f (cycles/sec)	Frequency.
L (in.)	Tunnel length.
l (in.)	Mixture-tube length.
n	Positive integer representing harmonic number.
p (lb./sq. in.)	Pressure of gases.
T (°K)	Temperature.
γ (dimensionless)	Ratio of specific heats of gases at constant pressure and constant volume.
λ (in.)	Wavelength.
ρ (lb/cu. in.)	Density of gases.

Subscripts

o	Room temperature conditions.
1	Combustion chamber temperature.
c	Including end correction.

III ACOUSTICAL THEORY

Before discussing theoretical considerations and results of tests, it is first necessary to define certain acoustical terms and some aspects of standing-wave theory. Terms that may be clarified by illustrations are denoted on the figures, and the terminology section describes and defines the various expressions used in the theory.

Terminology

1. Period (t).—Time interval for completion of one cycle.

2. Frequency (f).—Number of cycles occurring in 1 sec. Hence $t = 1/f$.

3. Cycle.—Complete sequence of values of pressure; at the end of a cycle, the pressure and rate of change of pressure together repeat themselves.

4. Amplitude.—Maximum magnitude of difference between instantaneous static pressure and ambient pressure in a given period.

5. Wavelength (λ).—Distance between two successive wave fronts in which the pressures have a difference in phase of one complete period. Hence $\lambda = ct = c/f$.

6. Standing wave.—Oscillations having a fixed distribution of amplitudes in space, characterized by the existence of nodes and antinodes that are fixed in space.

7. Nodes.—Points, lines or surfaces (of pressure, velocity or displacement) of a standing-wave system, which have zero amplitude.

8. Antinodes.—Points, lines or surfaces in a standing wave where there is maximum amplitude.

9. End correction (e).—Length added to an oscillating gaseous system to account for the fact that a pressure node at an open end is located at a point beyond the physical end of the system. The magnitude of correction depends on the configuration of the opening. For a cylindrical pipe, the correction is approximately $8a/3\pi$, where a is the radius of the tube.[2]

The first system to be considered is the open organ pipe or half-wave tube of Figure 1. A standing pressure wave in this tube can be visualized as follows :—

An initial movement of air from each end towards the centre creates a higher pressure at the centre of the pipe. As the pressure increases, the inflow of air decreases until it ceases and commences to move outwards because of the higher pressure at the mid-point of the tube. Owing to the momentum of the air, the pressure at the centre eventually falls below ambient pressure, and, with the build up of this partial vacuum, the outflow of air decreases to zero and reverses to repeat the cycle. The mode of oscillation is sinusoidal, both in time and along the tube in space.

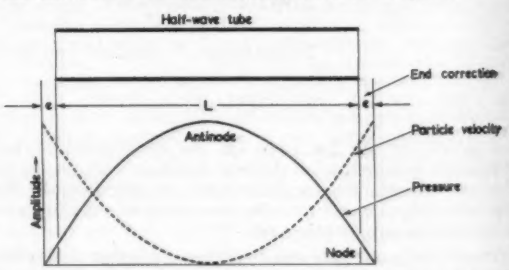

Figure 1.—*Standing Wave in an Open-ended Pipe.*

Figure 1 shows the sinusoidal variation of pressure along the length of the tube. The variation of pressure with time is shown in Figure 2.

The period, or time for one cycle of pressure variation in an open organ pipe is

$$t = 2(L + 2e)/c = \lambda/c \quad \ldots\ldots\ldots\ldots \quad (1)$$

Since the corrected length of the tube is equal to half the wavelength, the system is termed a half-wave tube. If the pipe depicted in Figure 1 were regarded as two half-wave tubes,

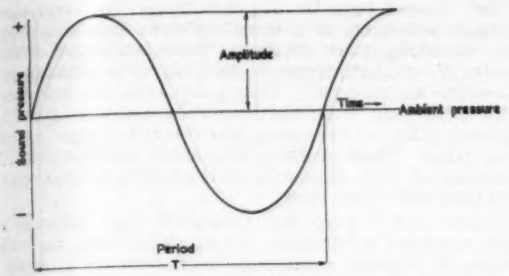

FIGURE 2.—*Sinusoidal Variation of Pressure with Time.*

each of length $L/2$, coupled at the centre, the pressure distributions along its length would be given by Figure 3.
The period of oscillation of this system is half of that given by equation (1) and the frequency is consequently doubled. The frequency of oscillation of the pressure distribution of Figure 1 is termed the fundamental or first harmonic

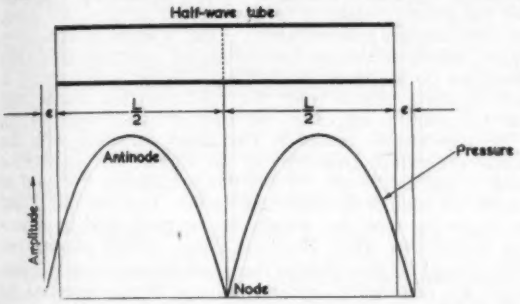

FIGURE 3.—*Second Mode of Oscillation of an Open-ended Pipe.*

frequency, that of Figure 3, the second harmonic, and so on. Hence, from equation (1), the expression for the frequencies of an open pipe are given by the relation :—

$$f = \frac{nc}{2(L + 2e)} \quad \ldots\ldots\ldots\ldots\ldots \quad (2)$$

n being an integer representing the harmonic or mode number. It is possible to have several harmonics sounding together in an open tube.

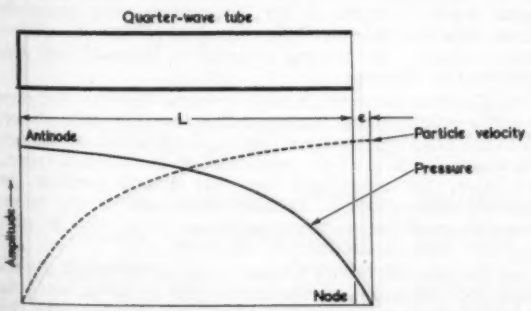

FIGURE 4.—*Standing Wave in a Pipe Closed at One End.*

Figure 4 shows the standing pressure wave in a pipe with one closed end. The pressure distribution and gaseous motion are the same as for one half of Figure 1. In other words, the half-wave tube could be divided into two quarter-wave tubes by a central division, consequently the expression for the period is :—

$$t = \lambda/c = 4(L + e)/c \quad \ldots\ldots\ldots\ldots \quad (3)$$

and the harmonic frequencies are given by :—

$$f = (2n - 1)c/4(L + e) \quad \ldots\ldots\ldots\ldots \quad (4)$$

The Effect of Temperature on the Velocity of Sound

Due to the fact that, in a tunnel burner assembly, the gases upstream of the combustion zone will be at ambient temperature, whereas the combustion products in the tunnel may have a temperature of over 2,000°K, it is necessary to know the effect of temperature on the velocity of sound, before corrections can be applied to the wavelength of the standing waves in the system.

To calculate the speed of sound in air at low temperatures, the expression :—

$$c = 1087{\cdot}42 + 1{\cdot}99T \text{ ft/sec} \quad \ldots\ldots\ldots\ldots \quad (5)$$

may be used[3], where T is the temperature in °C. This gives a figure of 1,127 ft/sec as the velocity of sound at 20°C. However, where the temperature differs greatly from 20°C, as in the burner tunnel, it is necessary to use the expression

$$c = \sqrt{\frac{\gamma P_1}{\rho_1}} = \sqrt{\frac{\gamma P_1 T_1}{\rho_o T_o}} \quad \ldots\ldots\ldots\ldots \quad (6)$$

The symbols used are listed in the nomenclature.

IV OSCILLATIONS IN COMBUSTION SYSTEMS

Of all the types of thermo-acoustic phenomena, a term that includes singing flames, gauze tones, rough burning and " screech " in rocket motors, the one that is most commonly observed is the " organ-pipe " oscillation defined in Section III. This is the type in which the wavelength of the sound emitted is related to the axial dimension of the burner, usually the path of gas travel through the inlet pipes, combustion chamber and exhaust system. It is relatively easy to determine whether an oscillation is of the organ-pipe type, since the product of length and frequency is nearly constant. After temperature corrections are made, theoretical and observed frequencies usually agree reasonably well.

It has been shown that this mode of oscillation is typical of the noise generated by ducted burners and other combustion systems of similar configuration[4, 5, 6, 7, 8] and several theories have been proposed to account for the mechanism whereby the sound is generated.

Among the many difficulties that prevent an accurate determination of the driving mechanism responsible for a given type of oscillation are the following :—

(i) A theoretical mechanism, or two or more mechanisms acting simultaneously, must be proposed to account for the presence of discrete frequencies. Predictions must be made and data obtained to check these predictions.

(ii) It is difficult to resolve a combustion system into components in order to make it mathematically tractable.

(iii) In all cases, it has been noted that the amplitude of oscillation tends to rise to a finite level, indicating that a mathematical analysis would need to include non-linear quantities. Hence, it is necessary to deal with infinitesimal oscillations and to determine whether they will increase or decay.

(iv) Any theoretical assumption that includes considerations of a time lag between the injection and combustion of the fuel in the combustion chamber will give rise to mathematical predictions of oscillations being driven under certain conditions. Acoustical damping terms must be included at some stage of the analysis.

The concept of standing waves in a burner assembly is easily explained, since, when air is forced through any duct, one or more of the natural modes of resonance of the duct are invariably excited to a certain degree. In the case of a ducted burner, the presence of the flame provides a source of energy to drive or damp the standing waves.

A method of driving standing waves by heat addition was first noted by Higgins[9] in 1802, and later by Rijke[10]. Subsequently, other authors have postulated explanations of the Rijke tones, including Lord Rayleigh[11], who defined a criterion whereby flames drive a standing wave. It is only recently that exact mechanisms for the driving of a standing wave by heat addition have been described in any detail, and, in all the considerations of organ-pipe oscillations reviewed here, the Rayleigh criterion is used. This hypothesis states that, for a heat-driven oscillation to occur, there must be a varying rate of heat release having a component in phase with the varying component of pressure. The point of heat addition must also be other than a pressure node in the standing wave. Although this criterion has been questioned where high average gas velocities and large rates of heat release are involved, its use has proved satisfactory in practice.

From considerations of the Rayleigh criterion, an intermittent source of energy is implied, which drives the oscillations and hence overcomes the damping forces in a combustion system. The oscillations in the burner will not reach a high intensity unless energy is added periodically to the gases in such a way as to meet two requirements. Firstly, depending on the type of energy being added, the periodic energy release must be in phase with either the pressure or velocity fluctuations in the burner assembly. For this to be accomplished, the period of the driver must be close to some multiple of the natural period of the system, but not necessarily equal to it. This is the time condition for resonance. The second requirement is that the energy must be released near a point of maximum effectiveness. This means that energy in the form of a velocity disturbance must be added near a pressure antinode of the mode of oscillation being driven ; conversely, energy in the form of a pressure disturbance must be added near a velocity antinode. One or the other represents the space condition for resonance according to the Rayleigh criterion.

Putnam and Dennis[4] used the Rayleigh criterion in the case of organ-pipe oscillations in a multiple deep-ported burner within a combustion tube. The upstream system consisted of a plenum chamber, which was treated acoustically as a Helmholtz resonator. They showed that the combustion chamber could be considered as a driver that caused periodic variations in the flow rate through the burner ports. Resonance of the plenum chamber resulted in a periodic supply of combustible material to the combustion chamber, and, at a somewhat later interval of time, to the flame. The burning of the incremental pulses of inflammable mixture periodically issuing from the burner ports furnished energy to drive the oscillations if the pulses were in phase with the oscillating pressure components in the combustion tube. The phasing depended on a time lag factor that was a function of the mixture velocity through the space between the burner ports and the mean burning points.[5]

Berman and Logan[12] investigated oscillations in rocket motors and suggested that the high pressure part of the cycle will initiate combustion in previously unburnt mixtures, causing a fluctuation in the rate of energy release with consequent driving of the oscillations.

Ellis[13] showed that, for a rocket motor, the organ-pipe oscillation was more of a travelling wave than a standing wave. A strong pulse starting at the injection end of the chamber travelled the length of the duct, to be reflected and returned to the head end. During this cycle, the amplitude of the pulse was being continuously attenuated, and the weakened pulse, on returning, was found to trigger a new strong pulse. These Authors also noted chamber-pressure oscillations of large amplitude corresponding to organ-pipe oscillations of a closed tube.

Crocco[14] and Crocco and Cheng[15, 16] have advanced a theory requiring a variation in combustion time lag with pressure to explain organ-pipe oscillations in a rocket. They showed that the time lag cannot be constant if the pressure varies, and developed a formula correlating them. Theoretical treatment showed that instability could arise even for a constant rate of fuel injection.

The apparatus of Howland and Simmonds[17] was more like a conventional tunnel burner. They noted that, below a critical tunnel length, the noise frequency increased with decreasing tube length, but that above this critical length the frequency remained constant. They postulated a theory that the mixture takes a certain period of time to ignite, but burns rapidly after ignition. Thus, a series of explosions occurs, which forces an oscillation of constant frequency depending on the ignition time lag. If the tunnel length is short, ignition occurs when the fresh mixture reaches the open end, and the frequency increases with decreasing length. If the combustion pulsation frequency coincides with the natural organ-pipe frequency of the tunnel, the oscillations attain a high amplitude. From this hypothesis, it should be possible to have combustion oscillations that are not of the standing-wave type, but which will be reinforced by organ-pipe oscillations when the frequencies closely correspond.

Blackshear[18] has evolved a theory of flame-driven standing waves by employing one-dimensional flow equations to deduce the laws governing the transmission, reflection and amplification of waves approaching a flame front. This analysis reveals the important parameters controlling the ability of the flame to drive or damp an oscillation. Waves pass through the flame front with their velocity amplitude unaltered, and, when the resulting net velocity causes a change in flame area, waves are propagated simultaneously into the gases upstream and downstream of the flame. If these flame-generated waves are phased with the existing components of the standing wave, they act as drivers ; when opposed, they damp the standing wave. From the flow equations, Blackshear has derived an expression for the ratio of the magnitudes of the upstream and downstream propagated waves in terms of the temperature ratio across the flame zone and the inlet Mach number. When this derived ratio is unity, the driving criterion is identical with that proposed by Rayleigh.

It is evident, from this review of recent theories, that there is still a wide disparity in the conclusions of different authors as to the exact mechanism of driving combustion oscillations. However, in view of the variation of combustion systems discussed, the indications are that several methods are feasible, depending on existing conditions in the burner assembly, and that a generalized theory is unlikely to apply to every form of combustion oscillation.

In the case of tunnel burners utilizing premixed gaseous fuels, the indications are that oscillations are governed by the Rayleigh criterion, since the flame and, consequently, the point of maximum heat release, are near the " closed " end of a combustion tube where the maximum pressure amplitude of any standing wave is found. In addition, standing waves in the mixture supply pipework are, under certain conditions, likely to be excited by oscillations in the tunnel. These

would lead to periodic variations in the rate of fuel supply and, hence, heat release, resulting in a reinforcement of the standing waves in the downstream section

V SMALL-SCALE BURNERS

(A) EXPERIMENTAL

In order to investigate theories of the mechanism of driving of tunnel-burner oscillations, a series of " tunable " single-port burners was constructed. These burners had parallel tunnels of variable length connected to fixed-length mixture tubes. Sintered alumina tubes with the best circular cross-section were selected for the tunnels, and lagged with asbestos rope. The tunnel length was varied by sliding an " Agalain " nozzle, cemented to the mixture tube, along the refractory tube. A gasket of asbestos string was wound round the nozzle, to ensure a gas-tight seal with the alumina tunnel. The tunnel and mixture-tube diameters were chosen so that their ratio was as near as possible to the optimum ratio for maximum pressure efficiency as proposed by Francis.[19]

During initial tests on these burners, it was noted that standing waves of high intensity occurred in the gas and air supply lines when the burner resonated, indicating that these oscillations were a contributory factor to the mechanism of reasonance. In order to predetermine the acoustic termination of the upstream length, a plenum chamber lined with sound-absorbing material was, therefore, connected to the end of the mixture tube. Owing to the effect of day-to-day variations in the quality of town gas, it was decided to use ethylene as the combustible. Ethylene and air were metered by a capillary flow gauge and a rotameter respectively and mixed at a mixing tee before being passed into the plenum chamber through a flame trap. Stoichiometric mixtures were used and the flow was held constant for a value of Reynolds Number = 10,000 in the mixture tube. The apparatus is shown diagrammatically in Figure 5.

Three sizes of tunnel burner were constructed, of the following dimensions :—

Tunnel Diameter (D) (in.)	Port Diameter (d) (in.)	d/D	Divergence from Optimum (per cent)
1	2	3	4
0·375	0·215	0·573	6
0·44	0·279	0·634	3·9
0·78	0·466	0·597	2·1

A mixture-tube length of 24 in. was chosen to ensure that the flow at the burner port approximated to fully developed turbulent pipe flow at Re = 10,000.

When making noise measurements, the tunnels were fixed and the upstream section moved by a micrometer clamp attached to the mixture tube. This gave an accurate control and measurement of the tunnel length.

The burners were mounted in an anechoic chamber 9 ft × 6 ft × 6 ft, lined with acoustically absorbent fibreglass quilt to ensure that all noise measurements could be made in approximately free field conditions without objectionable interference from sound reflections.

Readings of the sound pressure level were obtained by using a calibrated condenser microphone mounted at 90° to the tunnel exit and 20 tunnel diameters distant from the the burner axis. The microphone was connected to a Brüel and Kjaer type 2105 frequency analyser set to a linear response. All sound-pressure level readings were recorded in decibels based on a reference pressure of 2×10^{-4} dynes/sq. cm.

Noise spectra were obtained by recording the total noise on a tape recorder, *via* the condenser microphone. The recordings were then mounted on an endless-loop cassette and replayed, the output of the tape amplifier being connected direct to the frequency analyser. Where required, minor corrections were applied to the data obtained, to compensate for the non-linear frequency responses of the microphone, tape and preamplifier of the data-reduction system. Where it was only necessary to determine the peak frequency of resonance and its harmonics, this procedure was not deemed essential.

In all cases, the burner was allowed to heat up to its equilibrium working temperature before taking any readings, since

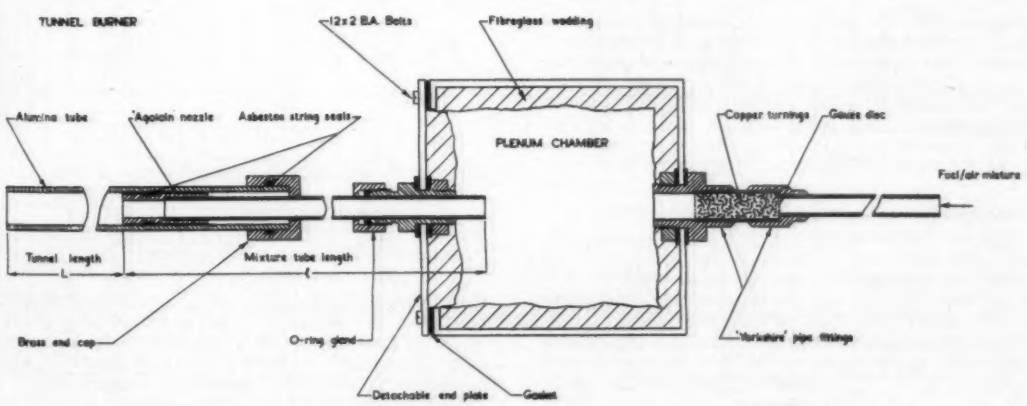

FIGURE 5.—*Experimental Burner with Upstream Acoustic Termination.*

it was found that the noise level decreased during the warm-up period.

(B) Results

Examination of the spectra of tunnel burner noise illustrated in Figures 6 and 7 shows that, as the tunnel length is increased, two maxima in the curves coalesce and form an intense narrow frequency band with associated higher harmonic frequencies. Figure 8 indicates how, when the burner is resonating in this manner, the overall sound-pressure level rises to a maximum and drops again to the quiescent noise level when the tunnel length is further increased. Thus, it is evident that, over a short range of tunnel lengths, some criterion for the driving of oscillations is satisfied, as will be shown by analysis of the spectral content of the noise.

In Table 1, the values of the discrete frequencies of each spectrogram are tabulated against the tunnel lengths, successive maxima being given subscripts 1, 2, 3. . . . Note that these subscripts do not indicate that the frequencies are necessarily harmonics.

Considering the spectrum of the noise generated by the burner with a 5 in. tunnel, there are several discrete frequencies present, superimposed on the broad random spectrum. The lowest frequency component (f_1), in the region of 800 c/s, is present in all subsequent spectrograms as the tunnel length is increased up to resonant condition. It is postulated that this note is generated by the combined lengths of the mixture-tube and tunnel soundings together, the low-amplitude oscillations being maintained by the requisite frequency component of the random noise spectrum.

Table 1

Tunnel Length (in.)	Discrete Frequency (c/s) 1st (f_1)	2nd (f_2)	3rd (f_3)	4th (f_4)	5th (f_5)	5th (f_5)
1	2	3	4	5	6	7
1		3,750	5,700			
1·5		3,850	5,500			
2		3,420	6,200	9,800		
2·5		3,200				
3		2,550	6,600			
3·5		2,050	6,000	10,000		
4		1,830	5,700	9,100		
4·5	835	1,780	4,850			
5	820	1,550	4,320	7,200		
5·5	810	1,300	4,100	6,700		
6	810	1,280	4,000	6,500		
6·5	805	1,240	3,680	5,950		
7	800	1,025	3,220	5,450		
7·5	797	985	3,160		7,150	
8						
8·5	877	1,760	2,650		4,850	6,150
9	865	1,745	2,580	3,470	4,360	

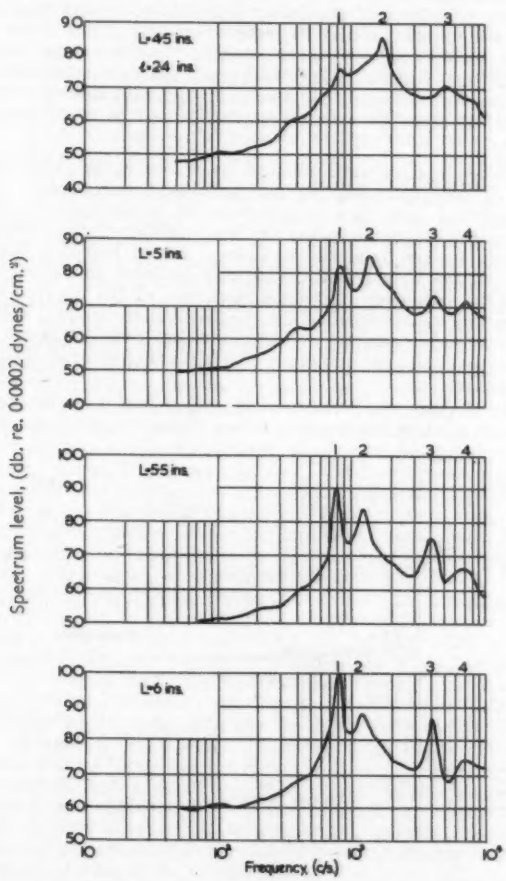

Figure 6.—*Frequency Spectra of Tunnel Burner Noise.*

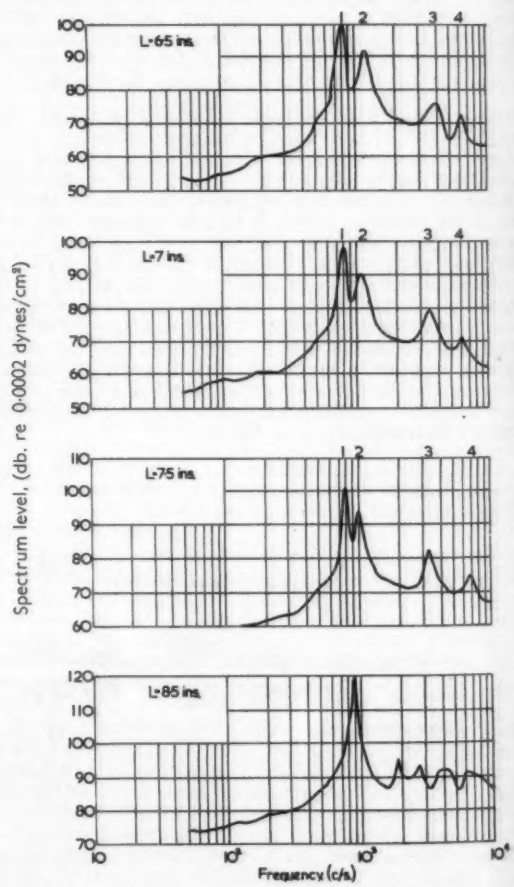

Figure 7.—*Frequency Spectra of Tunnel Burner Noise.*

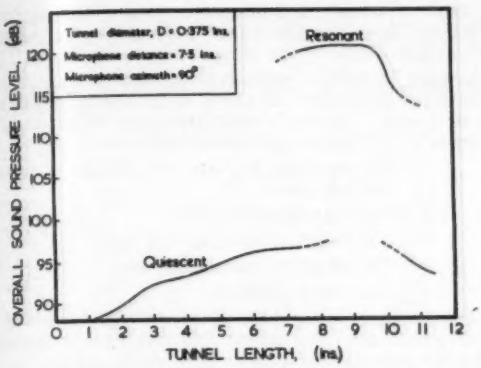

FIGURE 8.—*Variation of Noise Intensity with Tunnel Length.*

Proof of the existence of these standing waves was obtained by a survey of the dynamic pressure distribution along the mixture tube. A series of small pressure tappings was made at 1 in. intervals along the upstream section, and the sound pressure within the tube measured with a probe microphone attachment. A typical standing-wave pressure distribution is shown in Figure 9, indicating that the system is oscillating at its third harmonic frequency.

Equation 2 gives, having corrected for the change in sound velocity with ambient temperature :—

$$n = \frac{2f(l_c + L_c)}{c_o} \quad \ldots\ldots\ldots\ldots \quad (7)$$

where $l_c = l_0 + \frac{8a}{3\pi}$ and $L_c = L_0 + \frac{8A}{3\pi}$.

Substituting the values of f_1 from Table 1 in equation (7), a value of very nearly 3 is obtained for n, supporting the findings of the standing-wave pressure survey. Inaccuracies arise, since it is not known whether high temperatures affect the magnitude of the end correction ; also, no account was

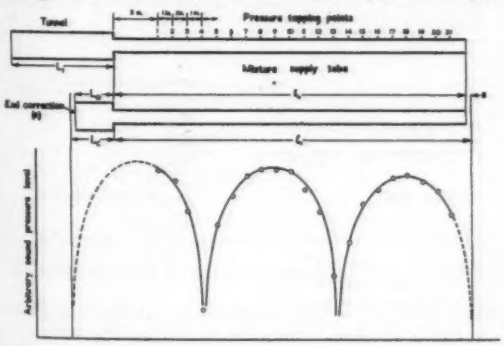

FIGURE 9.—*Standing-wave Pressure Distribution in Mixture Supply Tube.*

taken of the change in sound velocity due to either the presence of ethylene in the upstream mixture or to the composition of the combustion products downstream.

The discrete frequency (f_2) in the 1·5 Kc/s region, which occurs in the spectrogram of the 5 in. tunnel, has associated harmonics f_3, f_4 at frequencies of about 4·5 and 7·5 Kc/s. As the tunnel length is increased, the f_2 peak recurs with reduced frequency and increased amplitude, accompanied by two or more harmonics. Since the harmonics are successive odd multiples of the fundamental, the presence of quarter-wave oscillations of the tunnel is indicated in accordance with equation (4).

Substituting the condition for the first mode of oscillation of equation (4), in the expression for the velocity of sound given by equation (6), an expression for the average temperature in the tunnel is obtained

$$T_1 = \frac{16Lc^2f^2To\ \rho o}{\gamma P_1} \quad \ldots\ldots\ldots\ldots \quad (8)$$

Values of T_1 obtained from spectrogram data range between 1,400°K and 1,950°K, which are of the order expected for this type of tunnel, thus providing some confirmation that quarter-wave standing waves of the first mode are present.

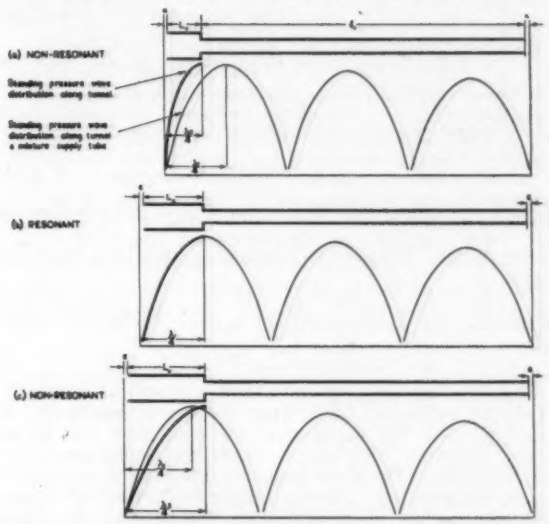
(a) NON-RESONANT
Standing pressure wave distribution along tunnel
Standing pressure wave distribution along tunnel & mixture supply tube
(b) RESONANT
(c) NON-RESONANT

FIGURE 10.—*The Conditions for Resonance of Burner Tunnel and Mixture Tube.*

The combination of quarter-wave and half-wave standing waves for the non-resonant condition will be similar to that shown in Figure 10a and 10c. In this diagram, the tunnel length has been corrected to its equivalent length at ambient temperature, according to the approximate relationship :

$$L_c^1 = L_{c4}^{1/7}\sqrt{\frac{290}{T_1}} \quad \ldots\ldots\ldots\ldots \quad (9)$$

From Figures 10 and 11, it can be seen that, as the value of f_2 approaches f_1, a point is reached where the antinode of the half-wave standing wave at the burner port becomes very close to the antinode of the quarter-wave standing wave of the tunnel. At this point, intense oscillations of the system will be driven. As the tunnel length is further increased its frequency of oscillation f_2 will fall below f_1, and the antinodes will be separated by a distance such that resonance of the system is no longer driven.

From the foregoing considerations, it appears that the upstream conditions in a tunnel burner assembly exert a dominant effect on the generation of organ-pipe oscillations. Where there is a precise termination of the upstream dimension, whether an open end as with a plenum chamber, or a " closed " end with a valve, oscillations will occur at a frequency such that an antinode of the standing-wave pattern is situated at or near the source of energy (the flame) as laid down by the Rayleigh criterion.

Thus, where the upstream termination is closed, the burner will resonate when the ratio of the upstream length to the

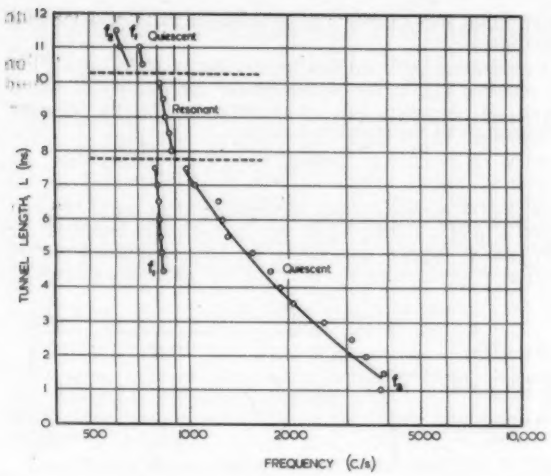

FIGURE 11.—*Variation of Peak Frequencies with Tunnel Length.*

tunnel length, corrected to ambient temperature, is in the region of

2 : 1, 4 : 1, 6 : 1 .....

When the upstream termination is open, the critical ratios are

1 : 1, 3 : 1, 5 : 1 .....

Since, for any standing-wave tube, a cut-off of the higher modes of oscillation exists when the quarter-wavelength is about equal to the diameter of the unit, there will be an upper frequency limit above which organ-pipe resonance will not occur. The lower frequency limit will be determined by the tunnel length. Between these two limits, oscillations will occur at the lowest frequency that satisfies the above conditions.

VI PERFORATED BACKPLATE BURNERS

It has been suggested that tunnel burners with perforated backplates are more prone to oscillatory combustion or "screeching" than single-port burners[19] Since this investigation is primarily concerned with noise production, it was decided to investigate the design of full-scale burners of this type.

A diagram of a simple perforated backplate burner, having a circular exit nozzle, is shown in Figure 12.

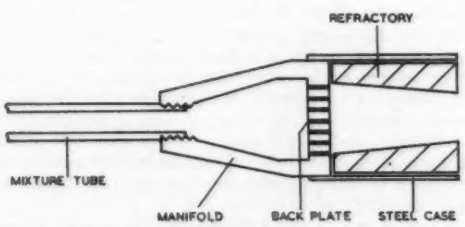

FIGURE 12.—*Typical Perforated Backplate Tunnel Burner.*

This kind of burner, and also those having rectangular or slot nozzles, have been developed and used at the Industrial Development Centre of the North Eastern Gas Board.[20]

The most important parameters in tunnel burner design appear to be the length and shape of the tunnel if resonance is to be avoided. Other factors exerting an influence on the combustion and, hence, the noise emission, may be :

(i) The number, size and arrangement of holes in the backplate.
(ii) The backplate thickness.
(iii) The length of the manifold box.
(iv) The length of the mixture tube.
(v) The tunnel material.

To conduct a systematic study of the effect of any one of the above factors required a burner that permitted each component to be interchanged without affecting the others.

(A) EXPERIMENTAL

The construction of the experimental burner is shown in Figure 13. The manifold box and mixture tube were lengths of 2 in. and 1 in. gas pipe respectively, connected by a reducing bush, thus permitting any variation in length of these two components. The steel back unit (3 in. square × 1¼ in. thick) had a hole through its centre threaded to take 2 in. gas pipe, the small flange serving to locate the perforated backplate. A sheet steel case was welded to the back unit, the length being determined by the required tunnel length. A suitably shaped steel core was inserted through the hole in the back unit, and a cold-setting castable refractory rammed in. The core was removed when the initial "set" had occurred, leaving the desired tunnel shape. The castable refractory used in all cases was "Purocast". The backplates consisted of 2 in. diameter steel discs of the required thickness drilled with the desired hole arrangement. By screwing in the manifold box, the backplate was pressed against the flange in the back unit. This design enabled the backplate to be changed readily ; it did, however, operate at a higher temperature than normal because of lack of conduction cooling.

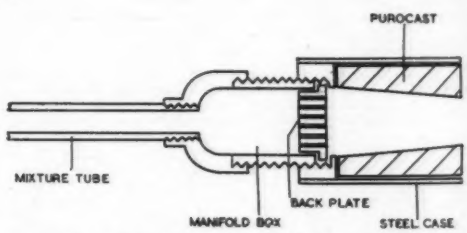

FIGURE 13.—*Experimental Perforated Backplate Burner.*

The air was supplied by a compressor having a large reservoir to avoid the slow surges that were found to occur in the fan air supply. The air and gas were separately metered, and mixed with venturi injector.

The factors thought to influence noise production were varied in the following way :—

(a) *Tunnel Length*

Five tunnel lengths were tested, namely 6, 5, 4, 3 and 2·5 in., and in each case the same core was used. In this way, the length of the parallel portion, before the converging nozzle, was varied.

(b) *Tunnel Shape*

Three cores were employed, each having the same general shape shown in Figure 13. The length of the 10° taper was,

however, altered to give nozzle exit diameters of 1·1, 1·3 and 1·5 in.

The range of tunnels constructed is summarized in the following table :—

Series	Nozzle diameter (in.)	Tunnel length (in.)				
1	2	3	4	5	6	7
A	1·1	6	5	4	3	
B	1·3	6	5	4	3	2·5
C	1·5	6	5	4	3	2·5

(c) *Number and Arrangement of Holes in Backplate*

The array used in most of the tests consisted of 91 holes of 0·1 in. diameter, arranged in rows to form a hexagonal pattern. A second design of 57 No. 30 drill-size holes was also made.

(d) *Backplate Thickness*

Three 91-hole backplates were used, their thicknesses being 0·5, 1·0 and 1·5 in. Some tests were also carried out with two 57-hole plates, 0·5 and 1·0 in. thick.

(e) *Manifold Box Length*

This was 2 in. long for most of the noise tests, but an 18-in. model was also used when the acoustic feedback upstream of the backplate was being measured. The effect of filling the 18-in. tube with sound-absorbing material was tested.

(f) *Mixture Tube Length*

In this preliminary series of tests, the mixture tube was 6 in. long. A duplicate tube with pressure tappings at 0·5 in. stations was also used to obtain feedback plots.

(g) *Tunnel Wall Material*

All the tunnels used so far were made from " Purocast ", but it is proposed to try a porous castable material.

The apparatus for measuring sound pressure levels and frequencies was described in Section V. The condenser microphone was placed in the same horizontal plane as the burner at an angle of 45° to the exit nozzle and 3 ft distant from it. Owing to the large heat release rates involved, it was not possible to conduct the tests in a sound-absorbing enclosure, and a large room (76 × 32 × 20 ft) was actually used. Although this room was acoustically " live ", the relative noise levels should not be affected.

In the initial series of experiments, it was decided to maintain constant manifold box and mixture tube lengths and

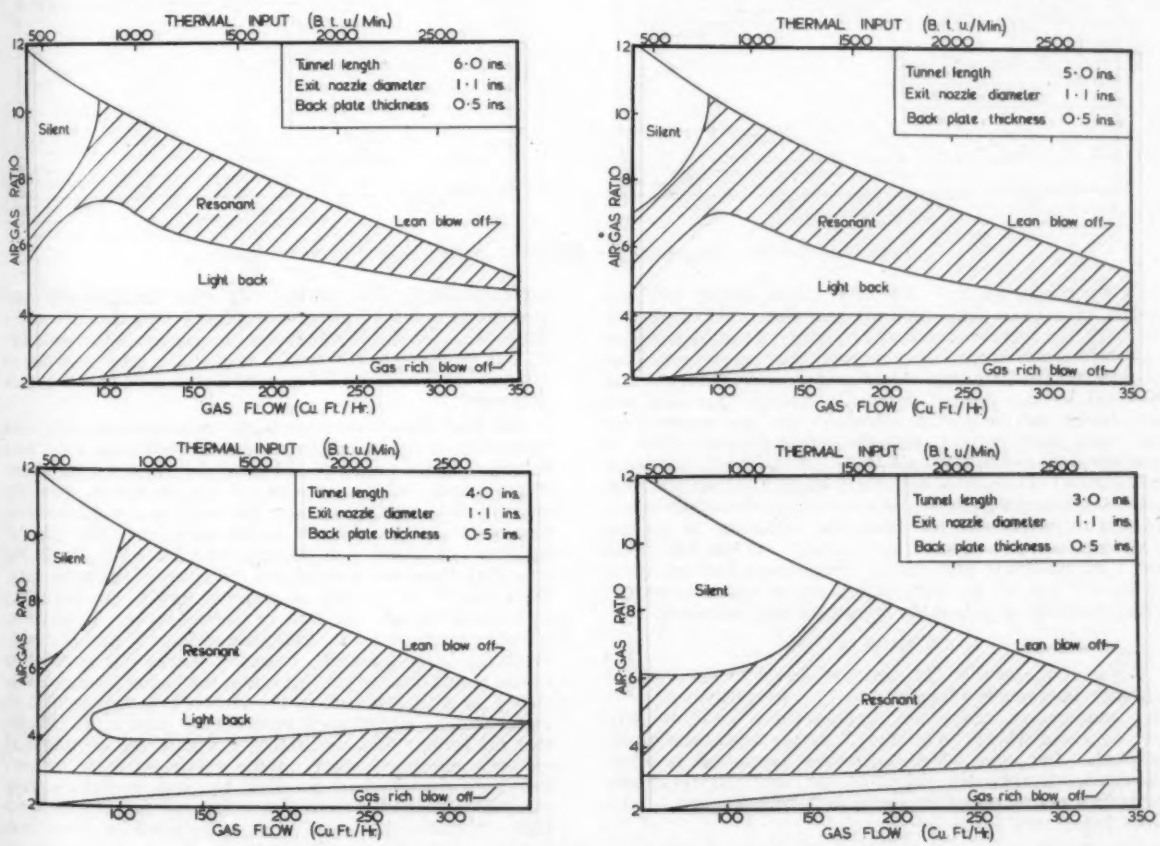

FIGURE 14.—*Stability Diagrams for Series A Burner with 0·5 in. Backplate.*

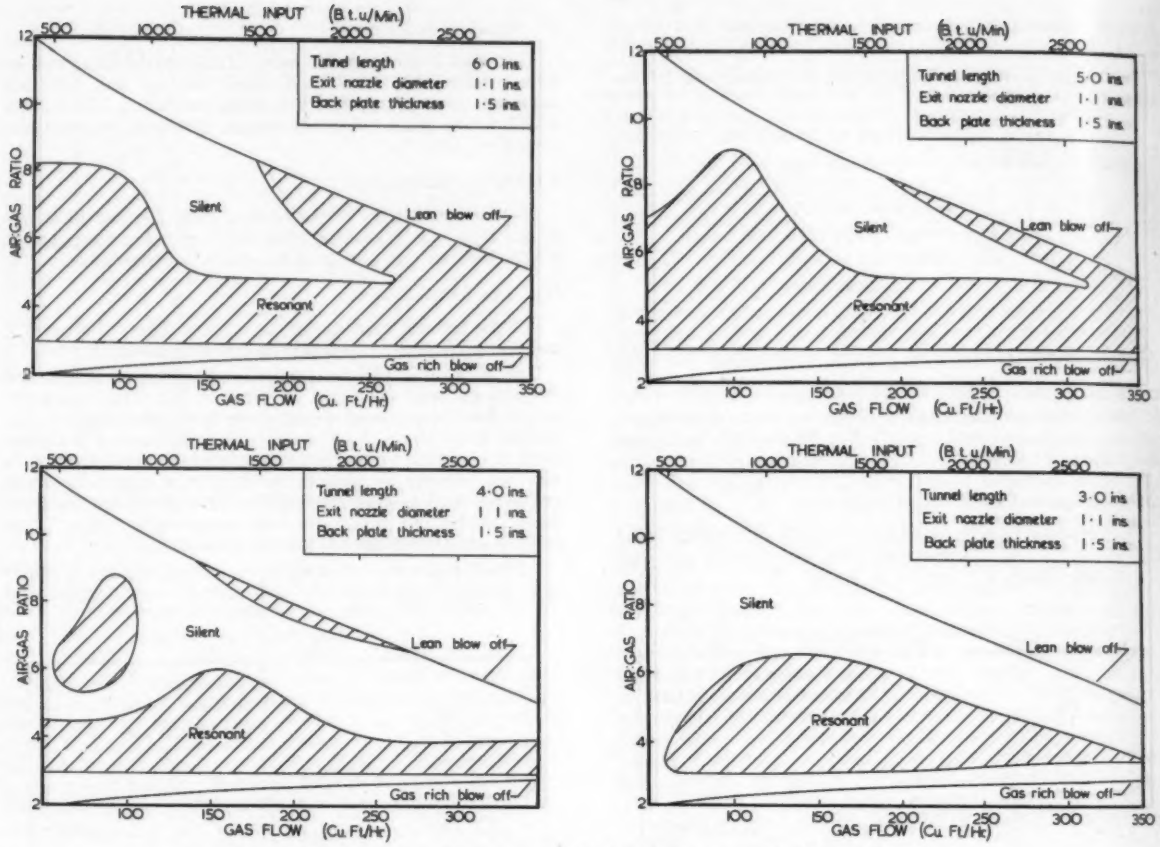

FIGURE 15.—*Stability Diagrams for Series A Burner with 1·5 in. Backplate.*

vary the tunnel lengths. For each tunnel length, measurements were made with different backplate thicknesses. In all cases, the tunnel was allowed to reach operating temperature before taking readings. A particular gas rate was then chosen and the air supply varied in increments from the lean blow-off to the gas-rich blow-off. Another gas rate was established and the process repeated ; air : gas ratios *versus* gas rates were plotted, and the sound-pressure levels in decibels were marked at each point on the graph. When a complete set of results for one tunnel length had been obtained, the backplate was changed and a second set of readings taken. In this way, the effect of day-to-day variations in the gas composition was to some extent avoided. It was found that the 1 in. backplate gave results intermediate between those of the 0·5 and 1·5 in. thick plates, and it was not used, in order therefore to reduce the number of tests necessary.

(B) RESULTS

Some of the results obtained are shown in the form of stability diagrams in Figures 14 to 17. In order to simplify the presentation, noise-level readings have been omitted, but the areas where " screeching " occurs have been cross-hatched. The zones where the burner lights back are also indicated. Graphs are presented for four tunnel lengths of both series A and B burners, each with 0·5 and 1·5 in. thick backplates.

The results show a progressive reduction of the noise region as the tunnel length is decreased, the shortest tunnel in all cases being the quietest. It was, unfortunately, not possible to cast a 2·5 in. series A tunnel using the core with a 10° taper. Since this length was the quietest for series B and C, it is proposed to construct a core with a taper in excess of 10° and use it to cast a 2·5 in. tunnel with a 1·1 in. exit-nozzle diameter.

The long tunnels were obviously undesirable as they were very prone to resonance, and extremely high noise levels were recorded, in the region of 130 dB under the worst condition. These tunnels, when used with a 0·5 in. backplate, were also susceptible to light back at air : gas ratios near stoichiometric. Comparison of the relevant results also shows the effect of backplate thickness. In all cases where a 1·5 in. backplate was used, there was a significant reduction in the noise zone. With the 2·5 in. tunnels of series B and C, no resonance occurred at any air : gas ratio or thermal input. In addition, no tunnel using a 1·5 in. backplate suffered from light back. With the longest tunnels, however, it was not possible to obtain stoichiometric proportions at the higher flows, because strong acoustic feedback to the venturi injector modified its performance. Preliminary experiments seemed to indicate that the lengths of the manifold box and mixture tube had no very significant effect on the noisiness of the burner. Packing a specially long manifold box with sound-absorbing material appeared to have little effect on the acoustic feedback. Considerably more work is required on these lines in view of the results obtained with the model burners in Section V.

The second set of backplates, containing a smaller number of holes of larger diameter, was made to give the same total port area as the original set. Initial tests showed a tendency for these to be slightly quieter, but more prone to light back ; a final assessment must, however, await a full trial.

For comparison purposes, the 6 in. series A tunnel was tested with a single 0·75 in. diameter port, when it approximated to the type D3 of reference 19. Sound-pressure levels at different thermal inputs for this configuration are plotted in Figure 18 as curve (b). On the same graph are results for :—

(a) 3 in. tunnel having a large resonant zone.

(c) 2·5 in. tunnel and 1·5 in. backplate that did not resonate under any condition.

(d) An open flame established on a 1·5 in. backplate with no surrounding tunnel.

It will be observed that the quietest result was obtained with an open flame ; adding a 2·5 in. tunnel increased the sound-pressure level by 6 to 9 dB. This type of perforated backplate burner was quieter at all flows than the single-port burner. If the design of the burner allows resonance to occur, however, then it is much noisier than the single-port type. The type D3 burner appears to be fairly immune to screaming, and its noise spectrum is broad and random as opposed to the perforated type, which produces most of its noise when resonating at one or two discrete frequencies. The curves for non-resonating systems show a progressive increase in noise intensity with thermal input ; when resonance occurs, as in curve (a), this no longer applies and the noise may remain constant during a sixfold increase in thermal input, or even decrease.

VII DISCUSSION

Considerations of various theories of noise production in combustion systems leads to the conclusion that the " screech " of tunnel burners is due to a form of organ-pipe resonance. The presence of the flame, acting as an energy source to drive standing waves, suggests that Rayleigh's criterion should be applicable. The results obtained with the model burners in Section V seem to confirm this theory and also indicate the importance of acoustical feedback in the upstream direction. It must be pointed out, however, that the apparatus used represents a highly idealized system, since the upstream acoustic termination was precisely fixed. With more practical burners, on the other hand, the effect of injectors, manifold, *etc.*, on the acoustic feedback is not yet known and should certainly repay further study.

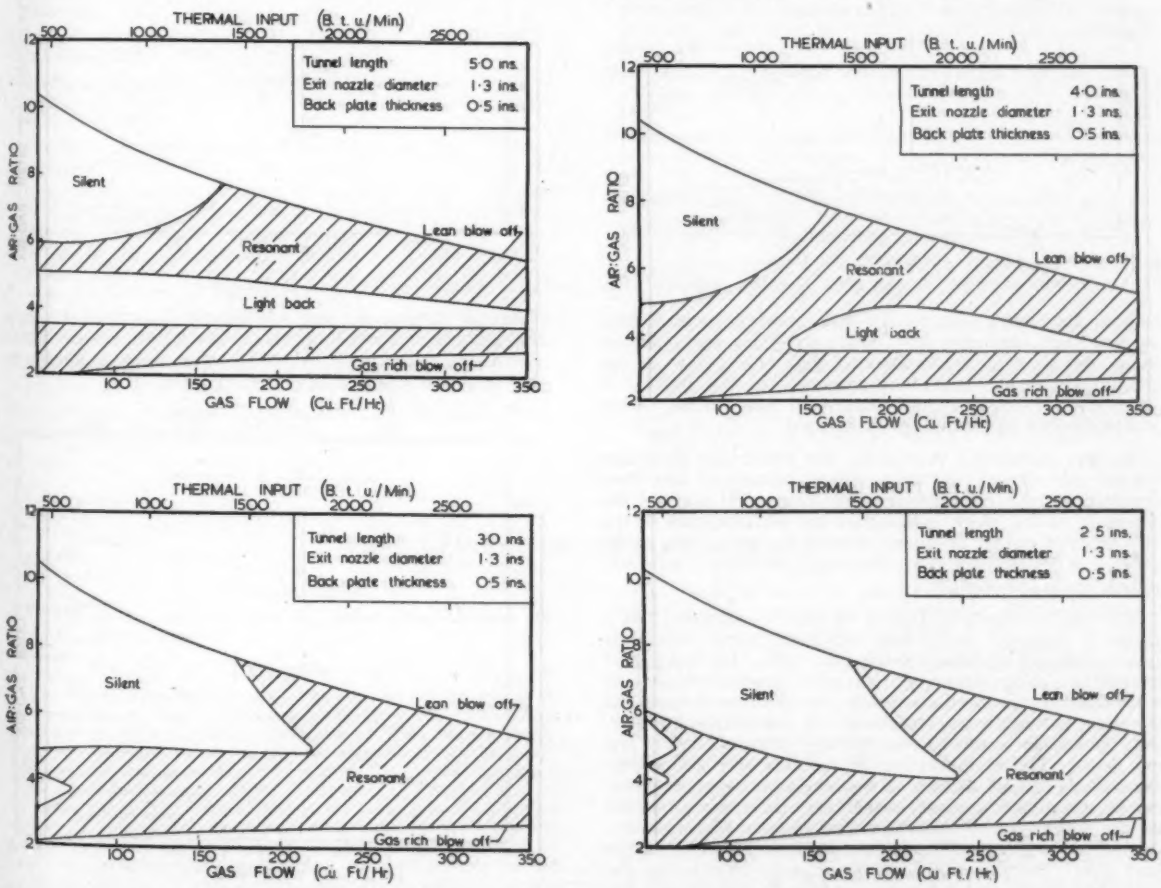

FIGURE 16.—*Stability Diagrams for Series B Burner with 0·5 in. Backplate.*

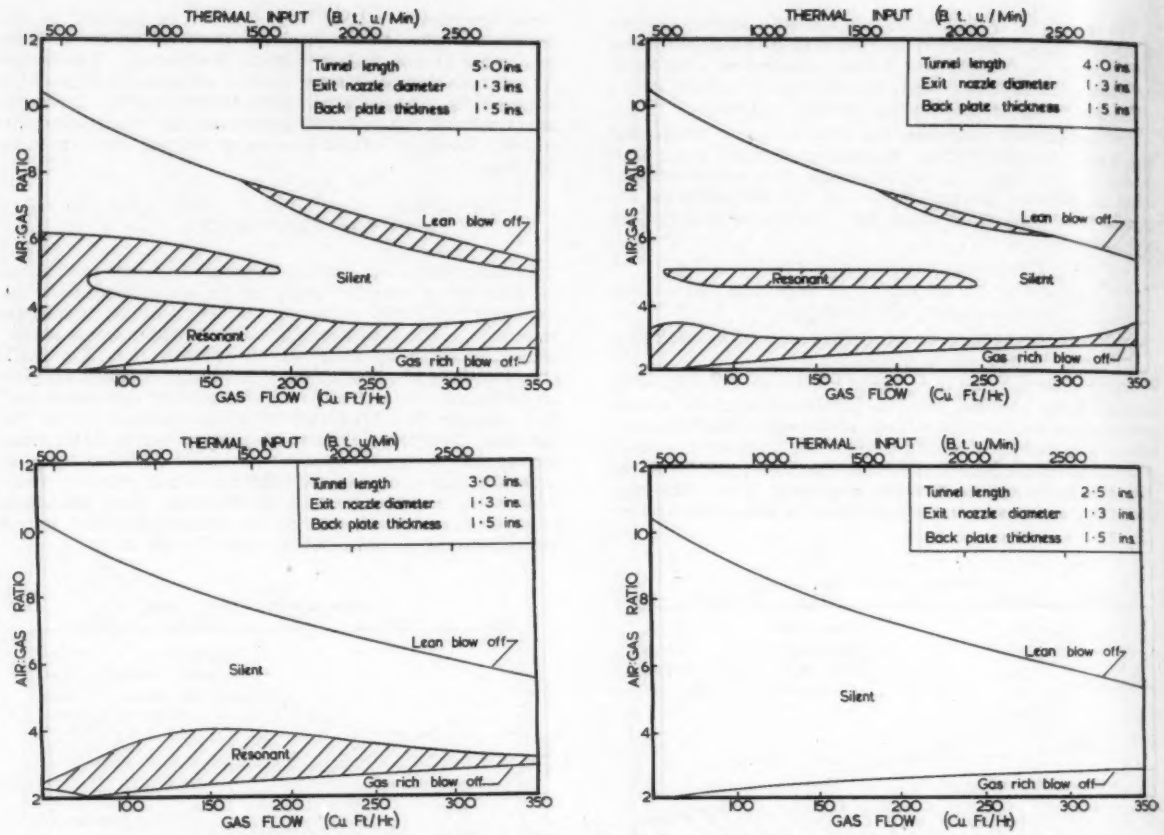
THERMAL INPUT (B. t. u./Min)
AIR:GAS RATIO
GAS FLOW (Cu. Ft./Hr.)
Tunnel length 5·0 ins.
Exit nozzle diameter 1·3 ins.
Back plate thickness 1·5 ins.
Lean blow off
Silent
Resonant
Gas rich blow off
Tunnel length 4·0 ins.
Exit nozzle diameter 1·3 ins.
Back plate thickness 1·5 ins.
Tunnel length 3·0 ins.
Exit nozzle diameter 1·3 ins.
Back plate thickness 1·5 ins.
Tunnel length 2·5 ins.
Exit nozzle diameter 1·3 ins.
Back plate thickness 1·5 ins.

FIGURE 17.—*Stability Diagrams for Series B Burner with 1·5 in. Backplate.*

The experiments with the full-scale burners would appear, at first sight, to have been conducted on a more *ad hoc* basis, but it must be emphasized that only a few of the preliminary results have been presented in this Paper. A large mass of frequency and sound-level data has been accumulated and is at present being analyzed.

As was mentioned previously, the perforated backplate burner was chosen for investigation because it has been reported as being very prone to resonance. It was not the intention of this work to compare the performances of the two types of burner or to recommend the use of one or the other. A few impressions on the subject would not, however, appear to be out of place.

The results shown in Figure 18 seem to indicate that a correctly designed, perforated backplate burner is slightly quieter than an equivalent single-port type. The single-port burner had a turndown ratio of approximately 10 to 1 at stoichiometric proportions, while the perforated type did not light back under any condition. It is not likely, however, that the burner would be required to operate with very low gas flows. The multiport burner requires only about one-third of the tunnel volume of the single-port type and thus can be made more compact, which may be an advantage for certain applications. With high flow rates of lean mixtures, it appeared to give more complete combustion than the single-port type. No assessment of the pressure drop across the perforated backplate was made, but there is little doubt that the burner would have a considerably lower pressure efficiency than the single-port type. With the same thermal input and using the same exit nozzle diameter, both burners should give a similar heating performance, since the gas temperature and discharge velocity should be comparable.

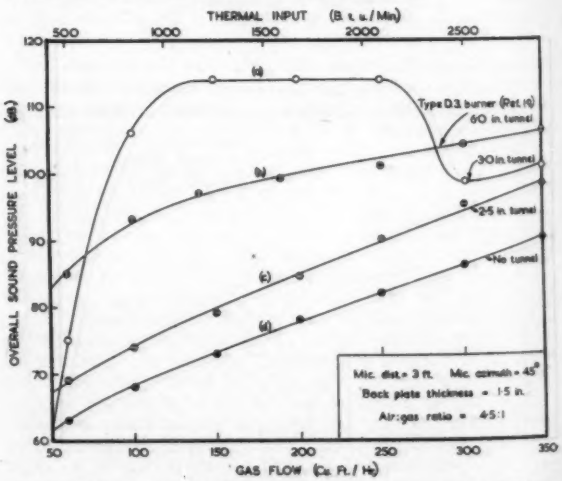
THERMAL INPUT (B. t. u./Min)
OVERALL SOUND PRESSURE LEVEL (db)
GAS FLOW (Cu. Ft./Hr)
Type D.3. burner (Pat. 19)
60 in. tunnel
30 in. tunnel
2·5 in. tunnel
No tunnel
Mic. dist.= 3 ft. Mic. azimuth = 45°
Back plate thickness = 1·5 in.
Air:gas ratio = 4·5:1

FIGURE 18.—*Variation of Noise with Throughput for Different Burners.*

The results obtained so far definitely indicate that, the shorter the tunnel, the less likely is the burner to be objectionably resonant. The optimum tunnel length for a practical burner must also take into account its heating efficiency, and further work is required in order to determine the best compromise. It would also appear that, the thicker the perforated backplate, the more silent will be the burner. The reason for this seems to be connected with the phasing of the upstream feedback, and experiments are being designed to elucidate the effect. The whole subject of upstream feedback and the nature of standing waves in the manifold and mixture tube is at present under investigation, together with the possibility of using some form of acoustical damper in order to neutralize the effect. Further analysis of the results already obtained should throw some light on the effect of burning velocity on noise production.

One difficulty encountered in any investigation of tunnel burners is that the flame cannot be readily observed. In order to overcome this, a scale model burner has been constructed with heat-resisting transparent windows. The techniques of high-speed photography and spark Schlieren photography will be employed in order to throw more light on the mechanism of noise production.

Acknowledgments

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PRESENTATION, DISCUSSION AND REPLY

Presentation

Dr. E. G. Jackson presented this paper for discussion and summarized its contents.

Discussion

Mr. W. E. Francis (Solihull).—Tunnel burner resonance is a phenomenon that can occasionally have a considerable nuisance value in particular applications. The more information that we have on the factors that control the incidence of resonance, the better able we shall be to predict resonance burner dimensions and avoid resonance in practice. The Authors' paper is, therefore, very welcome and timely, and they are to be encouraged to pursue their work with all possible speed. I have not always been able to see clearly where the work at Leeds was leading to, but I have no doubt whatever that the results of this investigation could have immediate practical use.

One ought to keep the noise problem in perspective. It occurs in only a relatively small number of applications. In fact, resonance screaming, as distinct from jet noise, occurs only in a very few cases. It is usually possible, by simple changes in the construction of a burner, to remove it. Once a burner has been put into a customer's appliance, however, alterations are awkward. In many instances, the mere fact that tunnel burners are sealed into an appliance is sufficient to muffle any noise that may be emitted, but no one would deny that there is still a problem to be solved.

The results reported by the Authors are broadly in line with experience at the Midlands Research Station of The Gas Council. In fact, the experimental work on parallel tunnel burners is very similar to work that we carried out on a tunable burner of 1 in. tunnel diameter fitted with an adjustable mixture tube, very similar in layout to that depicted in Figure 5 of the paper. The fuel was town gas rather than

the ethylene used by the Authors, and the mixture tube was the correct length for a type-A burner.

It was found possible to plot the peak frequencies as in Figure 11, though in the form of a contour diagram of the the sound levels in decibels. On the diagram referred to, it was possible to observe a strong resonance at a tunnel length of $8\frac{1}{2}$ in., which can be interpreted as an interaction of a quarter-wave tunnel resonance with the second harmonic of the mixture-tube resonance. This appeared, with a similar resonance, in the Authors' burner, in which the quarter-wave resonance of the tunnel coincided with the third harmonic of the mixture-tube resonance. On the diagram, at a greater tunnel length, there are signs of a further strong peak, which may represent interaction with the first mixture-tube harmonic. At higher frequencies, the first tunnel harmonic is discernible, although, in fact, there is no interaction with a mixture-tube harmonic, and hence no strong peak corresponding to the tunnel second harmonic.

Unfortunately, the Authors' experiments with a tunable burner have been carried out with long mixture tubes, which are unlikely to be used in practice. Consequently, in the Authors' experiments, alteration of the tunnel length had practically no effect on what might be called the "total length" frequency, denoted by f_1. The effect of tunnel length on this resonance is still further reduced when the tunnel length is corrected to allow for the increased velocity of sound in the tunnel.

When the length of mixture tube is 10 to 12 diameters, as used in practice, the corrected tunnel length is an appreciable proportion of the total length, so that, when plotting a diagram such as Figure 11, the f_1 resonance has a much greater slope and may not meet the f_2 tunnel resonance except at large tunnel lengths, which one would avoid in any case. Similar diagrams must obviously be drawn for larger burners, in which the whole diagram would be expected to shift towards lower frequencies. I recall what was said in another discussion, that the burners that people want to use now are quite large. The problem lies in the application of the work now being discussed to these much larger burners. From the burner designers' point of view, it will be necessary to develop a quick procedure for determining the most likely tunnel lengths for strong resonance, and then, of course, to avoid them. I think that this means the plotting of a diagram of the type shown in Figure 11, showing all the harmonics below the cut-off frequency. Experiments will obviously have to be carried out on a wide range of burner sizes and types to check such a procedure.

Coming again to the effect of burner size, in practice we normally do not use a definite acoustic termination, but an injector, which may be a commercial type, or fabricated from a standard "T". In either case, it is quite possible for the acoustic pressure waves to travel down the gas supply pipe. In the gas supply line, it is likely, in fact almost certain, that there will be mechanical devices such as governors and flap valves, which may resonate in sympathy with the burner, especially on large types, when the frequency of oscillation may be expected to be rather low.

If this does take place, and I strongly suspect that it has in one or two installations that I have seen, it is possible that the gas throughput may be momentarily cut off completely, with a subsequent reignition in the tunnel of an explosive nature when the gas supply opens up again. This has the effect of making the resonance seem very harsh. The higher harmonics would be greatly enhanced and the nuisance value of the noise, so far as anyone near the appliance might be concerned, would be very great indeed. This type of feedback has to be considered, and the Authors' suggestion for acoustic dampening in the manifold might have to be looked into very seriously.

At Midlands Research Station, we have attempted a form of acoustic dampening on experimental burners with a tunable side arm—coming from the entrance to the mixture tube—and have been able to dampen out completely particular resonances. Whether it will be a practical method remains to be seen.

Turning to the experiments with perforated backplates, it is disappointing to find a rather empirical approach, which many workers will feel merely duplicates their own experience. I know that this is an interim report, and I think that we may hope to see a more fundamental approach in any future work. I would invite the Authors to look again at the published work on combustion oscillations—not naturally gaseous combustion—in an attempt to achieve a fundamental approach. The mathematical aspects will be rather formidable, but these should not be shirked. It is an admirable subject for a department such as the Authors are in to take up.

It is well known that the resonance in this kind of burner may often be eliminated by a suitable choice of tunnel length—usually a very short tunnel, though I might point out that in furnace use one has almost always to penetrate the thickness of the brickwork, which is unlikely to be less than 9 in. If a very short tunnel length is used under these circumstances, the backplate is going to be well into the furnace wall and one would have to take steps to ensure either that the material is of a nature such as to stand the temperature, or that cooling is going to be added.

*Research Communication GC68** gives an example of a stability diagram showing zones of resonance for a typical perforated backplate burner. It is unfortunate that the Authors have not given frequency spectrograms, which might be matched up to this type of stability diagram. Apart from quoting overall sound pressure levels, no analysis of the acoustics of the system has been attempted. This will have to be done, I am quite sure.

Finally, I should like to draw attention to the fact that the design principles laid down in previous papers from the Midlands Research Station, apply to all types of air blast tunnel burners, and our position is neutral in any controversy between the use of various types of mixture feed. I think that a burner must be chosen on its merits, having regard to the job that it has to do. If it happens to be a perforated backplate type, then it should be used. Controversy on this kind of matter does not really help; one should have a flexible approach to the whole subject.

The Authors have whetted our appetites on this subject and we look forward eagerly to their future contributions. They should be encouraged by all industrial engineers who are in a position to help them and give advice. I welcome the paper.

Mr. G. W. Robertshaw (Manchester).—As one who is concerned directly in utilizing research information in preparing equipment designs, I have been very encouraged to see that increasing emphasis is being placed on the presentation of practical information based on an adequate test programme supported by a theoretical analysis.

Three papers on aspects of burner design have been presented at this 26th Autumn Research Meeting. All have had a direct practical use. We have even been advised that in order to carry out a particular modification to a manufacturer's product a small lathe may be used! I am not being sarcastic; I mention it to illustrate that the Authors have ventured very much into the practical field. Probably, they have witnessed the manner in which some of the suggestions may be carried out and have thought it worth while to give detailed guidance.

Multi-hole burner design appears to be in for a mass attack at the hands of the Midlands Research Station and the University of Leeds. May we hope that liaison between the two will ensure an absence of overlapping, and the maximum output.

There are a number of points in the paper on which I would appreciate some comment. Some of the tests on multi-hole burner stability diagrams illustrate areas at which light-back has occurred. Since the area of the individual mixture tubes is only in the region of 0·1 in. diameter, and the gas throughputs are considerable, this result cannot be reconciled with the results from the paper on stability, or with the results from multi-hole burners already in manufacture using the same hole diameter. Could the Authors say whether light-back occurred as a result of resonant combustion?

Several lengths of burner tunnel have been tested and it has been found that the shortest have given the best results.

*The Stability of Air Blast Tunnel Burners. Francis, W. E., and Hoggarth, M. L.

This corroborates the findings previously made, which have already been discussed. It has been found that a tunnel length in the region of 2½ to 3 in. is adequate for small-diameter mixture tubes, and that at these lengths the burners are free from resonance, but obviously have a considerable amount of ejection noise.

I should like to know whether the Authors contemplate greater attention being given to length, or whether they will concentrate on short tunnels. Mr. Francis has already made the point that in furnace application the length of burner tunnel, if very short, can have a nuisance value in overheating burner nozzles, which have to penetrate quite some way into furnace walls. I have considered this factor and made several test installations with thermocouples in order to investigate this aspect of the problem. I have found that, provided there is the merest flow of air/gas mixture, amounting to 1/10th or 2/10ths pressure in the burner manifold, there is no trouble whatever in this respect. The trouble occurs when an appliance is turned off, or one or other of the burners in a working installation is turned off.

So far as tunnel formations are concerned, apparently it is intended to concentrate on converging tunnels, since the maximum pressure efficiencies and velocities can be obtained by this means. Is it intended to cover diverging tunnels? If not, I would suggest that there is an equal market for this type of burner, and that silencing is still a matter of trial and error, and could profit by investigation.

As an illustration, it has been found that a diverging circular tunnel 3 in. long must have an included angle of not less than 20° to prevent resonant combustion. If, however, the circular mixture nozzle is expanded into a slot with an outlet area of only 50 per cent of that of the circular diverging tunnel, the burner does not exhibit resonance. These apparently conflicting results must have a cause, and this the Authors may find in due course.

It has been noted with great interest that increased backplate thickness is beneficial. From the manufacturing aspect, this could present difficulties and I would ask the Authors to exercise restraint. One hundred holes 1½ in. deep equals 12 ft 6 in. of drilling.

I would question a statement in the discussion concerning impressions about the relative performance of single *versus* multiple burners. It is suggested that the burner would not be likely to operate with very low gas flows. I have found that one of the chief advantages of multi-hole burners is their ability to operate at very low throughputs. As an example, I can cite a furnace with multi-hole burners, which operates on a maximum air pressure of 1·2 in. w.g. and an operating pressure of somewhere between 0·3 and 0·5 in. w.g. The complete unit, including the fan, makes less noise than some furnaces fired by low-pressure aerated burners.

It is also suggested that there is little doubt that the burner would have considerably lower pressure efficiency than the single-port type, but Mr. Francis has covered this point. So long as the area relationships are correct, there is no reason why pressure efficiency with the multi-port burner should be any lower than that with the single-port burner. I offer my congratulations to the Authors, and await their next paper with interest.

Mr. T. Ward (Dewsbury):—This is the second paper presented by Dr. Kilham and Dr. Jackson on this subject. It appears that great progress is being made and, even now, some definite practical results can be seen in the paper under consideration.

Research into a subject that contains many variables is obviously long and sometimes tedious. The variables in this particular subject are many, (i) tunnel length, (ii) tunnel form, and (iii) material of tunnel, backplate dimensions, thickness, material shape, perforation size and cross-sectional area.

Even external factors such as shape of combustion system both at hot end and mixing device all have their effect upon the noise produced by this type of burner. Resonance of great proportions, audible half-a-mile distant has been produced unintentionally during North Eastern Gas Board attempts to develop slot burners of moderate proportions.

Carrying out research into such an uncomfortable subject is not pleasant, and the preparation of the charts given as Figures 14, 15 and 16 must have been a marathon effort. The Authors are lucky they have not become psychologically unbalanced by their efforts. At Bradford, we plotted graphs in a similar manner to those represented in the paper, carrying throughputs to the intersection of the lean and rich blow-off lines; this occurred around 200×10^6 B.t.u./cu. ft heat release. We found that there was a zone of silence with all burners prior to reaching this heat input. One would think this was due to combustion towards the mouth of the burner giving a shorter effective tunnel length. I wonder if the Authors could agree with this thought?

The graphs in Figures 14 and 15 show the effect of backplate thickness. This appears to be of fundamental importance, showing that noise can be controlled without materially influencing burner performance.

What the industrial gas engineer is seeking from this work is the possibility of producing a virtually silent burner of any tunnel length to suit different burner situations, furnace wall thickness and feed-back of heat to the mixture behind the burner backplate. From the work so far, we appear to be in the position where we can prepare a noiseless combustion system with a 1½ in. backplate having a maximum tunnel length of 2·5 in. where we had previously thought of 2 in. Can we not modify our tunnel shape drastically, restricting combustion near the backplate?

In *Research Communication GC*68 by Mr. Francis and Mr. Hoggarth, we heard of troubles with light-back, and measures were suggested for reducing this difficulty, all of which appear to indicate a move in the direction of perforated backplates or towards systems where the flame front is in a controlled position; resonance was briefly mentioned.

It would appear that the ideal burner is of the perforated backplate type, not that with a small number of large mixture nozzles—in other words, a burner with a turn-down of something of the order of 50:1 to 100:1. With this we can be certain of consumer satisfaction, easy ignition and little fear of explosive ignition. A burner of this type has a full load pressure drop across its backplate of some 10 in. w.g. Now, we can tolerate this pressure loss only if we revise our methods of producing air/gas mixtures, and this is on the way.

Unfortunately, resonance has dogged the production of satisfactory burners of the highest combustion intensity, and I should like to congratulate the Authors and say that we look forward to the production of the perfect burner, which can be used to fill the gap now existing for a cheap jet burner of minimum proportions.

Mr. R. F. Hayman (London):—I am puzzled about two points arising out of this valuable work. As I said in the discussion on the paper by Francis and Hoggarth, we must resolve several diverse views in the planning of high-velocity burner installations.

There are customers' requirements, heat input, pressure levels of air and gas and optimum pressure efficiency coupled with stability of turn down, two factors sometimes difficult to reconcile with one another. After, or should it be before, comes the problem of noise. I seek the Authors' views on where this investigation of noise should fit in with the overall research investigation on tunnel burner design, since they do not yet appear to be able to indicate how we can translate work in simple short tunnel burners to divergent and convergent tunnels of optimum pressure efficiency, particularly in large-diameter burners where, for practical reasons, the burner tube may have to be longer than is theoretically desirable.

A further point is that ethylene requires about three times the volume of air for combustion, compared with town gas. Although, therm for therm, total heat output is the same in the burners studied, there must be some effect on the total volume of products, their temperatures and velocities. Do these different products have any appreciably different effect on the resonance of standing waves compared with the products of combustion from town gas, and can this difference, if any, be related to the effect in practice on burners using town gas? I ask this because, if one looks at the stability diagrams in Figure 14 and succeeding figures, the relation of gas flow to thermal input on the curves suggest that gas of a calorific value of 500 B.t.u./cu. ft was used. In the first part

of the paper, I am rather sad to see, the Authors say that owing to the effect of day-to-day variations in the quality of town gas it was decided to use ethylene as the combustible. However, we have to live with town gas and we must design burners to cope with these variations if they exist, but from the figures I have just mentioned the Authors appear to have gone to town gas for work on perforated backplate burners, but they do not say so. Am I right, and, if so, would the Authors please elucidate?

Written Contribution

Mr. L. T. Minchin wrote:—The tunnel burner with perforated plate is strikingly similar to one of the burners studied in the first set of systematic experiments on burner noise to be made by the gas industry in Britain. I refer to the work done at the National Physical Laboratory and reported in the former Gas Research Board's *Communication* GRB.3* I myself selected the gas burners used in this work, and, in addition to the practical commercial burners, I sent an experimental bunsen burner I had constructed, in which the familiar "Meker" grid was replaced by a thin perforated plate (200 holes, $\frac{1}{32}$ in. diameter). This burner, at 10 cu. ft/hr, emitted a piercing scream under some conditions, especially when first lit.

Dr. Constable and his colleagues at the National Physical Laboratory made a number of very interesting observations on this burner, although the whole project was dropped shortly after the outbreak of war. They found that the pitch of the note produced corresponded to the fundamental of the mixing tube; as the tube was lengthened, the note fell, till between 4·8 and 5·2 in. no sound at all was emitted. On lengthening still further, the noise reappeared on a higher note—the first overtone of the fundamental.

The evidence they produced suggests that the vibration was caused by the flames seated on the perforation of the flame port. The vibration of the column of air under the flame could be maintained by the energy of combustion; a particle of gas moving upward would enter the flame zone and so be expanded, while on the downward path it would be chilled and so contract; thus, the maintenance of the vibration would be accounted for.

Another interesting feature of the National Physical Laboratory report was that by placing a barrier around the air-port and some $\frac{1}{4}$ in. away, the noise could be silenced completely—presumably due to some interference phenomenon. Did Dr. Kilham and his co-workers find this worked with their burners? If so, do obstacles in the path of the flame have a similar effect? I think the work described in GRB3 is important and should not be forgotten.

Written Reply

The **Authors**, in reply, wrote:—The Authors would like to thank the contributors to the discussion for their interesting observations and suggestions for future work. It was gratifying to hear that the results obtained at the Midlands Research Station with a variable-length tunnel burner agree with the theory developed in Section V. When commencing the investigation of any complex problem, it is always good policy to attempt to reduce the number of unknown variables, hence the use of a definite acoustic termination in the preliminary series of experiments. The effect of using a commercial venturi injector or a fabricated parallel-tube injector will be studied in due course. Feedback of acoustic pressure waves down the gas supply line was encountered in the series of experiments with perforated backplate burners, but only in cases where the whole assembly was strongly resonant. From the results at present available, the indications are that the controlling length of the upstream system is the distance between the burner nozzle and the air nozzle.

The use of a tunable side arm as an acoustic damper, reported by Mr. Francis, has also been investigated by the Authors. The first results were quite promising, but later work showed that, although it was possible to damp out a note of given frequency, sometimes another resonance took its place; i.e., the effect of the damping tube was to change the pitch of the scream. The positioning of the tunable side arm along the mixture tube is also to some extent critical, since it should coincide with a pressure antinode in the standing wave. The best position acoustically appears to be just behind the mixture nozzle, but this would quite frequently be inconvenient to arrange from a practical point of view. The method may, however, justify further investigation.

Although no frequency spectrograms for the perforated backplate burners have been presented, these were naturally obtained while compiling the results for the stability diagrams. Acoustical analysis of the system was not completed in time for the presentation of the paper.

The Authors have no intention of entering into any controversy regarding the use of single-port or perforated backplate burners. As Mr. Francis stated, each has its applications.

The light-back zones referred to by Mr. Robertshaw are due to the high amplitude oscillations during resonant combustion driving the flame back through the backplate perforations.

The necessity of developing silent burners with long tunnels is appreciated by the Authors, and every effort will be made in this direction. It is not the intention to concentrate on parallel and converging tunnels only; the reason for the choice of parallel tunnels for the first series of experiments is that the acoustic theory of cylindrical pipes is well understood whereas very few data are available on the standing-wave pattern in diverging pipes. Tunnels with a high degree of convergence may also have to be treated as Helmholtz resonators instead of closed-ended organ pipes.

The effect of increasing the throughput to the intersection of the lean and rich blow-off lines reported by Mr. Ward, has not been obtained in our laboratories, since the requisite pressures were not available. The theory that the silence zone is due to the combustion zone moving towards the burner mouth, thus giving a shorter effective tunnel length, may well be correct and indicates the necessity of developing some method of observing the behaviour of the flame inside the tunnel.

The Authors do not agree that the ideal burner must necessarily be of the perforated backplate type, and they repeat that the type of burner must be chosen with reference to its intended application.

In reply to Mr. Hayman, it must be stressed again that this is purely an interim report, and it is not reasonable to expect the inclusion of full design data for every conceivable type of tunnel burner. The results of noise investigations may quite well mean that some pressure efficiency must be sacrificed in order to obtain a non-resonant burner.

With reference to the use of ethylene, the main effect as compared with town gas is that the effective tunnel length will be changed owing to the different temperature and density of the combustion products. There appears to be no reason why the volume of the products *per se* should have any effect on the theory of resonance, provided that it is divorced from the possible influence of combustion intensity. As mentioned previously, ethylene was used in order to reduce the number of variables in the system during the investigation of the basic mechanism of resonant combustion.

The Authors confirm that town gas was used in the experiments with perforated backplate burners.

Mr. Minchin recalls the work on a modified Meker burner described in *Gas Research Board Communication* GRB3. The Authors do not agree that this burner is similar to the perforated backplate burners of Section VI since no tunnel surrounded the flame. The most likely explanation of the whistling note is that the shedding of vortices from the edges of the perforations led to a periodic fluctuation of flame area, which could drive oscillations in the mixture tube. It is unfortunate that insufficient data were presented to allow the calculation of Strouhal numbers to be made in order to check this theory.

The use of deflecting screens around the injector is not so easy to apply when using air blast injection as opposed to pressure gas injection, and has not, therefore, been attempted.

Ward[20] has shown that inclined baffles around the exit of a tunnel burner can reduce the noise, and the Authors agree that the effect may well be due to some interference phenomenon.

* *Trans. Inst. Gas Eng.* 1940-41, **90**, 265 to 294.

CURRENT DEVELOPMENTS OF THE GAS INDUSTRY IN FRANCE

By R. Odier

Director, Research Department, Directorate of Economic and Commercial Services, Gaz de France.

Communication No. 586

The following paper, illustrated by slides and a film, was presented by Monsieur R. Odier (Gaz de France) at special meetings of District Sections of The Institution of Gas Engineers, arrangements for which were made in collaboration with the Scientific Office of the French Embassy in London, and Gaz de France. The Institution expresses its warm appreciation to Monsieur Odier for the time and energy he kindly devoted to the preparation and presentation of his paper, and to all concerned with the organization of his visit for their cordial and helpful co-operation.

The programme of the meetings was as follows :—

Monday, 30th January, 1961	*Joint Meeting of the London and Southern and the Eastern Sections. (London.)*
Tuesday, 31st January	*North of England Section. (Newcastle-upon-Tyne.)*
Wednesday, 1st February	*Manchester and District Section. (Manchester.)*
Thursday, 2nd February	*Wales and Monmouthshire Section. (Cardiff.)*
Friday, 3rd February	*Midland Section. (Birmingham.)*

Notes of the discussions of the paper at these meetings follow the text of the paper itself.

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I GENERAL SURVEY

The French gas industry, which had remained static between 1920 and 1939, was in such poor condition that many people thought it obsolete at 6th April, 1946, at which date it was vested as a nationalized industry. War damage, increasing operating costs and tariff cutting hampered greatly the progress of gas sales and the improvement of the industry's finances.

At that time, too, privately owned gas undertakings controlled 591 distribution systems that distributed mostly coal gas produced either in isolated plants or in works linked by restricted transportation networks. (Figure 1.)

By the end of 1960, the distribution systems of Gaz de France, without having varied greatly in number, were as shown in Figure 2. The great development of the industry's transportation mains, and the closure of a considerable number of gas works, which have been replaced either by propane or propane/air stations or by cracking plants using petroleum products as feedstock (e.g., light distillates, refinery gases), are immediately noticeable. A comparison between the state of the French gas industry in 1947 and 1960 is made in Table 1.

Table 1

	Undertakings	
	1947	1960 (31st Dec.)
1	2	3
Conventional gas works	458	150
Coke oven gas supplied through a transportation network	123	150
Reformed natural gas	—	3
Straight natural gas	3	86
Cracked gas produced from liquid hydrocarbons, propane or refinery gas	—	32
Propane/air	—	106
Straight propane	7	66
Total	591	593
Length of transportation network (miles)	1,450	6,500

This development will undoubtedly continue as quickly as the modernization programme of Gaz de France comes into operation. In about two years' time, for instance, coal distillation will be confined probably only to coke

FIGURE 1.—*Disposition and Constitution of the French Gas Industry at the End of 1946.*

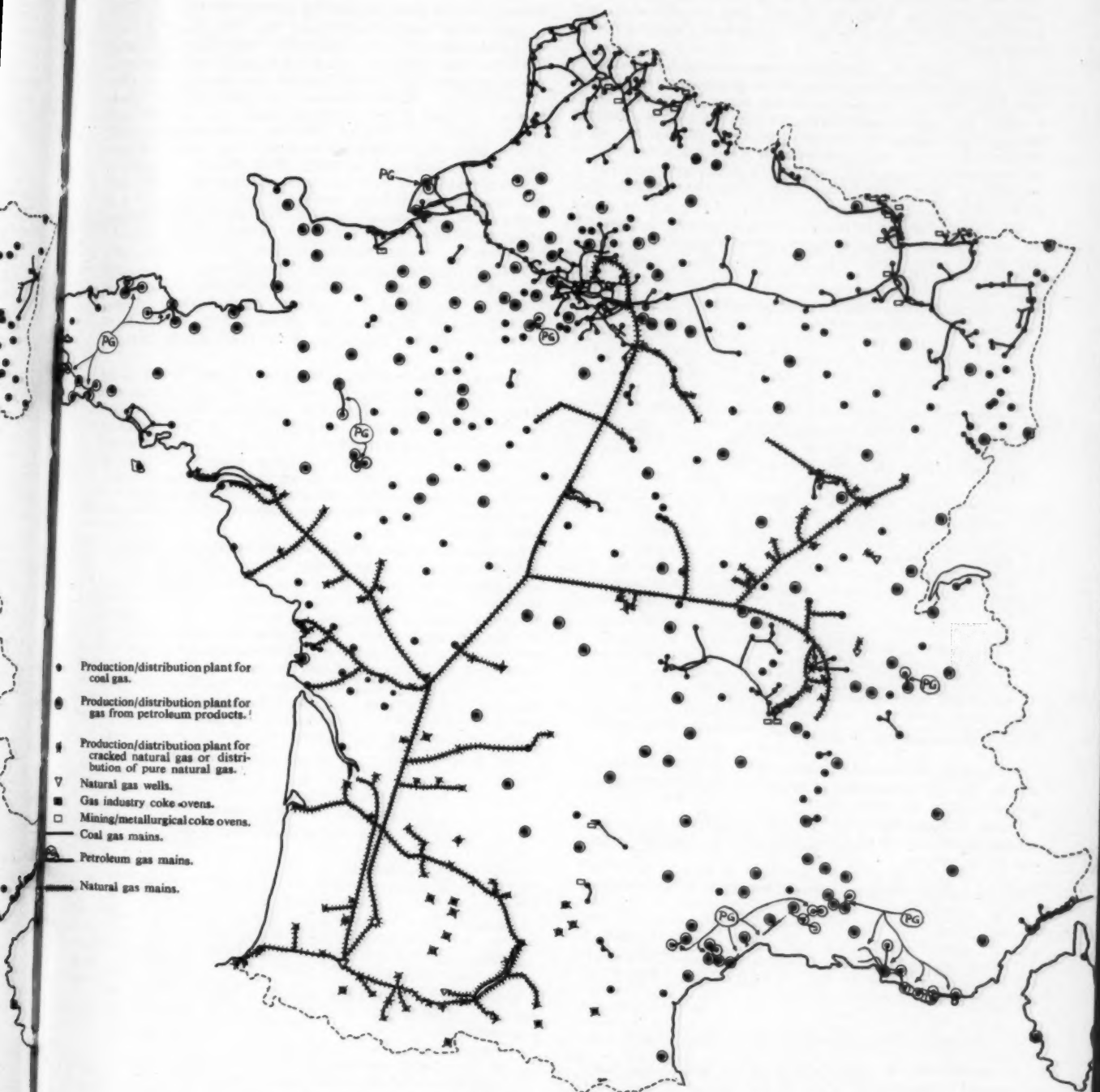
PG
Production/distribution plant for coal gas.
Production/distribution plant for gas from petroleum products.
Production/distribution plant for cracked natural gas or distribution of pure natural gas.
Natural gas wells.
Gas industry coke ovens.
Mining/metallurgical coke ovens.
Coal gas mains.
Petroleum gas mains.
Natural gas mains.

FIGURE 2,—*Disposition and Constitution of the French Gas Industry at the End of 1960.*

ovens located near Paris, Rouen and Strasbourg; the remaining distribution systems will be linked to a pipeline transporting coke oven, or natural, gas, or alternatively converted to the use of liquid or gaseous hydrocarbon feedstocks.

Table 1 shows the complete transformation of production technique that has taken place in France. Though this has lessened the gas-producing activities of Gaz de France, the gas-transportation activities of the National Service have increased considerably, and its part in the future will consist more and more in collecting gases from all available sources and transporting them to consumers located, in many cases, far away from their points of production.

Presentation of the technical evolution should, however, be accompanied by information about the parallel and prospective sales from 1947 to 1965. This is shown in Table 2.

TABLE 2.—*Gas Sales Development in France.*

	1947	1960*	Ratio 1960 to 1947	Prospects for 1965
1	2	3	4	5
GAZ DE FRANCE : Domestic consumers ..	4·481 mill.	5·540 mill.	1·23	6·150 mill.
Sales :	Mill. therms	Mill. therms		Mill. therms
Domestic	266·0	407·0	1·53	534
Commercial	36·0	89·5	2·50	145
Industrial	47·5	160·0	3·40	224
Various	22·2	20·0	0·90	25
Totals	371·7	676·5	1·82	928
S.N.P.A. and G.S.O.—CEFEM (subsidiary companies of G.D.F.-S.N.P.A.)				
Industry	21	423 } 786	37·5	730 } 1,300
E.D.F.	—	363 }		570 }

* Provisional figures.

G.D.F. Gaz de France.
E.D.F. Electricité de France.
S.N.P.A. Société Nationale des Pétroles d'Aquitaine.
G.S.O. Société Nationale des Gaz au Sud-Ouest.
CEFEM Compagnie Française du Méthane.

(These figures do not include the direct supplies by mining and iron works coking plants to their workshops and for chemical synthesis, which at present amount to approximately 330 mill. therms.)

From 1965, the development prospects of Gaz de France will be dependent essentially on the availability of natural gas.

Table 3 shows the part (in percentages) taken by gas (excluding that from blast furnaces) in the consumption of energy in France.

TABLE 3.—*Proportion of Gas in Energy Consumption in France.*

Sector	1947	1960	1965
1	2	3	4
	Per cent.	Per cent.	Per cent.
Domestic and Commercial	7	7	8†
Industrial*	4	13	17†

* Excluding electricity production and blast furnaces. † Estimated.

In actual fact, in areas where natural gas is supplied, gas already accounts for 25 to 30 per cent of energy consumption in the industrial sector. In the South West, which hitherto has not been greatly industrialized, this figure is above 60 per cent as a result of high demand by the chemical industry.

II THE ADVENT OF NATURAL GAS

The discovery and marketing of natural gas was the prime factor that led to the increasing activity of Gaz de France.

Just before the Second World War, two small deposits of natural gas, of local importance only, were worked in the Jura and supplied to Lons-le-Saunier and Amberien. Then, on 14th July, 1939, natural gas was discovered at Saint Marcet, Haute-Garonne, the reserves of which, located at 4,000 ft below ground level, were 230,000 mill. cu. ft. The war delayed effective development of this deposit until 1947 when Toulouse and Pau were first supplied; later, Bordeaux in 1952. This deposit of sulphur-free and extremely pure gas is more than half exhausted, but still makes available about 30 mill. cu. ft/day; it is a deposit of the hydraulic type and its well-head pressure is about 1,500 lb/sq. in. The gas is stripped of its gasolene at Boussens. Saint Marcet natural gas was regionally limited in importance to South West France.

In 1949, the Société Nationale des Pétroles d'Aquitaine (S.N.P.A.) discovered at a depth of about 2,000 ft at Lacq a small deposit of petroleum, which in 1960 supplied approximately 90,000 tons of crude oil fairly highly charged with sulphur.

Continuing its prospecting at greater depth, S.N.P.A. in December, 1951, struck, at about 11,000 ft, an accumulation of gas that from the beginning, unfortunately, proved to be very difficult to cope with: in fact, the Lacq gas contains approximately 15 per cent of sulphuretted hydrogen and 10 per cent of carbon dioxide; pressure in the structure is about 10,000 lb/sq. in, and the temperature 300°F. Taken together, these characteristics constituted a world record of problems to be solved before the deposit could be worked.

Because the effect of acid gas on the stressed metal of well tubing leads to breakage of the steel into pieces, an eruption occurred when the first well was bored. Though this was successfully dealt with, it was necessary to develop, before proceeding to exploit the deposit, steel and joints capable of resisting the acidic nature and the pressure of the gas. It was not until 1955, however, that a steel of these properties was produced at the Pompey-Vallourec-Schneider Steelworks. Exploitation of the deposit proved possible from that time, and the first unit of the purification plant that S.N.P.A. started to build in 1956 began to process gas at the end of April, 1957.

The progress (past and projected) of production is as follows: —

Period	Extraction of Crude Gas (Mill. cu. ft/day)	Pipeline Gas (Mill. cu. ft/day)
1	2	3
January, 1958	35	23
September, 1958	85	53
January, 1959	110	70
May, 1959	195	125
September, 1959	250	160
January, 1960	350	235
January, 1961	500	320
September, 1961	700	460

From this time, the Lacq deposit is expected to deliver, annually, 230,000 mill. cu. ft of crude gas to provide, after treatment,

50,000 mill. cu. ft of pipeline gas,
1·2 to 1·3 mill. tons of sulphur,
200,000 tons of high-octane petrol,
80,000 tons of propane, and
80,000 tons of butane.

Reserves recoverable from Lacq are at present estimated to be approximately 7·5 bill. cu.. ft, so that their exploita-

tion may be expected to last 30 years on the schedule indicated above.

Natural gas supplies will be divided amongst consumers approximately as follows, with 460 mill. cu. ft/day from Lacq, and 30 mill. cu. ft/day from Saint Marcet:—

Sector	Consumption (Mill. cu. ft/day)	Consumption (Per cent)
1	2	3
Electricité de France	150	30·5
Public distribution	130	26·5
Manufacturing Industry	210	43·0
Total	490	100·0

As a preface to consideration of the techniques of gas extraction and treatment, the percentage composition of Lacq crude gas is given in Table 4.

TABLE 4.—*The Percentage Composition of Lacq Gas.*

Constituent	Per cent
1	2
Methane	69·1
Ethane	2·8
Propane	0·8
Butane	0·6
Higher hydrocarbons	0·9
Sulphuretted hydrogen	15·3
Carbon dioxide	9·7
Mercaptans	0·05
Carbon oxysulphide	0·05
Water	0·7

Owing to the pressure drop in the gas in the tubing, the gas arrives at the well-head at 6,500 to 7,000 lb/sq. in, according to the output; its temperature is 180° to 200°F. At this point, the gas is expanded to 1,400 to 1,500 lb/sq. in; it requires also to be reheated, and is injected with glycol to inhibit the formation of hydrates in the collecting network; about 75 per cent of its humidity is eliminated.

The gas arrives at the processing plant at about 1,150 lb/sq. in and a temperature of 60° to 70°F. The baffle plates of a liquid separator strip the gas of its liquid hydrocarbons, and the crude gas passes on for desulphurization which is effected by washing it first with water and then with mono- or di-ethanolamine, and so on in series to ensure double washing.

Water in the main column at 1,050 lb/sq. in reduces the hydrogen sulphide/carbon dioxide of the crude gas from 25 per cent down to 10 to 12 per cent; the carbon oxysulphide content also falls to a low level. This water passes into a power recuperator in which, expanded to 140 lb/sq. in, it liberates gases rich in methane, carbon dioxide and hydrogen sulphide.

This gas is re-washed in a second column to recover the hydrogen sulphide removed. The water is sent to a stripper in which the dissolved hydrogen sulphide and carbon dioxide are separated by the introduction of deoxygenated flue gases. From the stripper, the released gases are forwarded to the sulphur plant, and the water, containing but small quantities of dissolved gas, is recycled from the bottom of the tower towards the main (first) column.

A second-stage di-ethanolamine washing is given at 1,000 lb/sq. in in a contact column, and a final soda wash eliminates the last traces of sulphur compounds.

The amine is regenerated in a column working at 20 lb/sq. in and 270° to 280°F; the acid gases are sent to the sulphur plant.

A part of the processing plant purifies crude gas directly with di-ethanolamine without first washing it; the final soda wash is then more rigorous.

The purified gas is dried and cooled in propane and ethane evaporators at 40°F and −100°F respectively; its temperature is brought to about −100°F, and the pressure lowered from 1,000 lb/sq. in to 650 lb/sq. in by direct expansion. The fluid then separates into two phases, (i) a gaseous phase that constitutes pipeline gas, sent to the network, after recompression, at 1,000 lb/sq. in, and (ii) a liquid phase made up of a mixture of ethane, propane, butane and petrol. Fractional distillation separates these products, and the ethane, obtained in fairly considerable quantities, is used in producing ethylene.

The recovery of sulphur from sulphuretted hydrogen is carried out by (i) the burning of a fraction of this gas in a steam generator to produce sulphur dioxide, (ii) then the reaction

$$SO_2 + 2H_2S \rightarrow 3S + 2H_2O$$

is brought about at 430° to 450°F in catalysis chambers charged with bauxite. The resultant sulphur vapour is condensed by producing low-pressure water steam in exchangers, and is sent to liquid-sulphur pits. The output of the sulphur works reaches 96 to 97 per cent.

Additional plant at Lacq includes (i) a steam-producing station of 672,000 lb/hr at 950 lb/sq. in gauge, (ii) a 1,500 kW thermal station, (iii) water-pumping and compressed-air plant, *etc.*, (iv) conventional propane storage for 175,000 gal, (v) refrigerated propane storage for 900,000 gal, (vi) an L.P.G. bottling section, and (vii) petrol storage for 5·5 mill. gal. This processing plant cost about 60 milliard francs (old).

The staff at Lacq numbers 1,200 to 1,300, half of whom work in three 8 hr shifts and half during normal day hours.

The corrosiveness of the crude gas (15 per cent of hydrogen sulphide and 10 per cent of carbon dioxide) and the high pressure at well-head (7,500 lb/sq. in) make permanent control of the plant and collecting network absolutely essential.

To guarantee full production from the deposit (700 mill. cu. ft/day), 30 to 40 wells will be necessary. Since wells are in some cases as much as 9 km distant from the plant at Lacq, a centralized radio control is able to investigate all the wells in approximately 60 sec. The following seven checks are carried out:—

(i) the smooth functioning of radio equipment,
(ii) the position of the first (main) valve,
(iii) the pressure in the annular space of the well,
(iv) the pressure at the head of the well,
(v) the position of the high/low shut-off valve that protects the low-pressure side of the plant,
(vi) the initial temperature of gas in the collector, and
(vii) gas pressure in the collector.

The control-room is equipped with (i) a geographical map on which the wells are marked by green signals that change to red in case of anomaly, and (ii) a board that, by means of a control-lamp, controls the above parameters for each well; this lamp flashes when a fault is detected.

Radio transmission is frequency-modulated in the 70 to 80 Mc/s band, the coded signal on the characteristic frequency of each "pit" causing the "pit" equipment to change to transmission while the control station goes over to reception. The well transmitter then transmits according to a programme synchronized with the control-room receiver, by which, in turn, the elements of the information are channelled to the appropriate detectors and signals. By these means, control is, in fact, continuous.

The collecting network is protected at approximately every 2 km, and at special crossings (road or river), by automatic safety valve and non-return flaps. At railway crossings over highways, canalization is made through

gas-tight tubes filled with nitrogen and fitted with a bursting-plate fixed to a ring. The closing of an automatic valve, or the raising of the pressure in a tube of nitrogen is notified by cable transmission to the radio cabin at the pit nearest to it, and the condition is controlled simultaneously with the elements of the well.

III TRANSMISSION SYSTEM

Following are some technical details of the mains and transportation facilities relating to the Lacq systems:—

The main arteries from Lacq to Roussines (24 in. diameter), from Roussines to Paris (20 in.) and from Rousines to Vindecy (18 in.) are of welded and expanded sheet-iron pipe, welded longitudinally; those from Vindecy to Lyon-le-Peage (16 in. to 12 and 8 in.), from Vindecy to Champvans (10 in. and 8 in.) and from Chazelles to Nantes (10 in.) are of extruded steel pipe; and the subsidiary branch lines generally are of 6 or 4 in. diameter.

The chemical and mechanical characteristics of the steel used are as follows:—

	Steel	
	A37 SHLE	X42
Carbon (max., per cent)	0·16	0·20
Silicon (max., per cent)	0·20	0·25
Manganese (per cent)	0·35 to 1	0·35 to 1
Phosphorus (max., per cent)	0·05	0·05
Sulphur (max., per cent)	0·04	0·04
Phosporus + Sulphur (max, per cent)	0·07	0·07
Rupture strength (*R*) (min., lb/sq. in.)	53,000	60,000
Elongation at rupture (*A*) (Min., per cent)	18	18
Apparent elasticity limit (*E*) (lb/sq. in.)	0·7 to 0·9*R*	0·7 to 0·9*R*

The pipelines were butt assembled and electrically welded.

The hydraulic pressure tests carried out at the works were at 1,070 lb/sq. in. for pipe diameters of 12 in. and above, and at 1,300 lb/sq. in. for those of 10 in. or less. In actual fact, the tests are made at 150 per cent of the service pressure (1,500 lb/sq. in.).

Before being put into service, the gas pipes are tested under hydraulic pressure 10 per cent higher than the service pressure (1,100 lb/sq. in.), and, to ensure their gas-tightness, they are subjected to a 10-day test at a minimum pressure of 100 lb/sq. in.

The pipes are coated externally with glass silk coated with coal tar or with bitumen to a minimum thickness of $\frac{1}{8}$ in. Internally, they are coated with "Inipol". Lining tests are carried out with an electric brush and at 10,000 V.

The embankment over the gas pipeline is 3 or 4 ft.

Particulars of the booster stations are given in Table 5:—

TABLE 5.

Station	Distance from Lacq (Miles)	Distance between Stations (Miles)	Maximum Throughput (Mill. cu. ft/day)	Compression Ratio	Installed Capacity (b.h.p.)
1	2	3	4	5	6
Auros	54	89	320	1·61	10,000
Chazelles	143		320	1·61	10,000
Roussines	223	80	280	1·34	6,000
Vindecy	360	137	150	1·33	3,300

The compressors, the total efficiency of which exceeds 35 per cent, are of the "right angle" reciprocating type, the cylinder motors being supercharged by turbo-blowers fitted to the gas exhaust. The plant equipment is as follows:—

Auros.—Five "Clark" sets by Dujardin of Lille, three cylinder compressors, six two-stroke cylinder motors in line, 2,000 b.h.p., 672,000 lb/min.

Chazelles.—Five Ingersoll-Rand sets (four from U.S.A. and one by C.A.F.L., Saint-Chamond), four cylinder compressors, 12 four-stroke cycle cylinder motors in V, 2,000 b.h.p., 739,200 lb/min.

Roussines.—Three sets identical with the preceding ones.

Vindecy.—Three Ingersoll-Rand sets by C.A.F.L., Saint-Chamond, two cylinder compressors, six four-stroke cycle cylinder motors in V, 1,000 b.h.p., 739,200 lb/min.

There is also a small, automatic power station on each plant, which works on some hundreds of kilowatts and is made up of two generating sets driven by gas engines. Staffs vary from 12 to 18, two-thirds of whom live locally.

IV CITY-GATE AND DELIVERY STATIONS

City-gate stations (Figure 3) are used to reduce the gas pressures in urban areas by 100 to 200 lb/sq. in. and in any case to reduce pressure to less than 350 lb/sq. in.

Delivery and metering stations guarantee to supply gas to the public and to industry at utilization pressures less than 80 lb/sq. in.

At the city-gate, the CD line is generally dispensed with, as well as the AB safety valve, the distribution pipes being capable of bearing the full pressure of the gas. In general, there is no metering.

In public utility supply stations, the CD line is sometimes identical with the AB line and automatically assumes its function in the event of breakdown.

Stations supplying industry are constituted as shown in Figure 4.

Equipment of the stations described is as follows:—

(i) The different block-valves are generally of the plug type, either conical or cylindrical. Throttle-valves are fitted with seats and clacks.

(ii) Filters: Cloth, felt filters, ceramic filters, cyclone, or multi-stages of these components.

(iii) Heaters: The temperature of the gas is not raised above 140°F. The low-pressure side temperature is regulated at about 45°F.

According to the power required, heating resistances or a hot water exchanger using gas in a boiler are used. The heaters are necessary when the pressure-drop exceeds 140 lb/sq. in; the power, which varies with gas delivery, ranges from 40,000 to 400,000 B.t.u./hr.

(iv) Regulators include a valve and a pilot regulator maintaining a steady, downward pressure. The expansion can be carried out in one stage only, between 1,000 and 50 lb/sq. in, approximately. The combination of two regulators and a diaphragm makes it possible to regulate the gas flow.

(v) Safety devices: Exhaust valves draw off gas to atmosphere if pressure rises abnormally; these are doubled with bursting aluminium discs, thin calibrated aluminium, or nickel foil.

Figure 3 shows an example of security control. Exhaust valves 1 and 2 work at 80 and 85 lb/sq. in. respectively. A disc bursts at 100 lb/sq. in., and the safety valve operates at 115 lb/sq. in.

(vi) Gas metering:

(*a*) Orifice meters with diaphragm are always placed after the regulator in the interests of constant pressure. The minimum diameter of the metering circuit is 24 in.; that of the diaphragm one-third the diameter of line D ($\frac{1}{8}$ in.). Precision required for the orifice diameter is 1/1,000. Differential pressure is registered on a chart thus showing output, and the consumption is found by planimeter.

(*b*) Volumetric meters are either of the dry diaphragm type working under pressure, or of the Delta type with revolving pistons. By connecting to a switch clock, it is possible to actuate a microbreaker or a photo-cell to produce impulses expressed as hourly output.

This plant is nearly always outdoors, the metering and regulating components being protected by a simple shelter.

V UNDERGROUND STORAGE

Two underground storage sites (Lussagnet and Beynes) are in operation; and one (Vernon) is in the pre-installation stage. Unlike comparable North American sites, these three structures never have contained hydrocarbons.

(1) Lussagnet

The Lussagnet storage was discovered and equipped by S.N.P.A., and is 35 miles north of Lacq. It is made up of a porous layer of 150 ft of sand, and its 1,500 ft thick cover of clay guarantees absolute gas tightness. The depth of this reservoir is about 1,800 ft, and the gas is stored at a pressure of 700 to 750 lb/sq. in. Storage capacity is 25,000 mill. cu. ft with an additional gas cushion amounting to a third of this. The water-drive of the structure is favourable, and the reservoir is equipped to ensure an output of 180 mill. cu. ft/day, which is balanced by input. As it leaves the wells, the gas is subjected to simple dehydration by triethylene glycol, and to recompression at 970 lb/sq. in, and is then sent to the transportation system with a dew-point of $-15°$ to $-20°$F. The virtue of this storage is that it is possible to work the processing plant regularly in spite of variable demand, and eventually to carry out maintenance at regular intervals, or to cope with accidental shut-down.

(2) Beynes

The Beynes reservoir, about 25 miles west of Paris, was discovered and equipped by Gaz de France and fulfills an entirely different requirement in that it regulates not the production of Lacq gas, but its transportation and also the rate of the production facilities in the Paris area in spite of considerable fluctuation in consumer demand. This represents about 40 per cent of the total sales of Gaz de France, the daily supply being, on average, about 140 mill. cu. ft; in the event of its being very cold, this can reach 350 mill. cu. ft (12°F). Unlike Lussagnet, Beynes at present stores manufactured (coke-oven or reformed natural) gas at 470 B.t.u./cu. ft, which posed entirely new problems to the technicians of Gaz de France.

The characteristics and equipment of the Beynes storage are as follows:—

(i) Storage layer: This is in the Lower Cretaceous Wealden sands at a depth of 1,000 ft below sea level; it is 100 to 115 ft thick, with 30 to 40 ft of clay cover; it has 25 to 27 per cent porosity, and 550 lb/sq. in. of hydrostatic pressure avoids recompression of the gas upon its being withdrawn.

(ii) The structure is equipped with 14 injection wells, two control wells, and seven wells for checking water level and assuring gas-tightness; compression capacity for injecting 35 mill. cu. ft/day of gas and raising the pressure to 650 from 245 lb/sq. in.; 140 mill. cu. ft/day withdrawal capacity. The total volume stored is 12,000 (at present 8,000) cu. ft, out of which 6,300 mill. cu. ft can be used every winter. The connecting pipeline for the transport network in the Paris area is 16 in. diameter. All equipment at the well-heads and of the collecting system are remotely controlled from a control centre.

(iii) Gas processing: Because it has been manufactured, the gas stored at Beynes has to be specially processed. (*a*) During injection, the removal of unsaturated hydrocarbons, which may generate gum and clog the wells, is done by activated charcoal which also retains phenol, benzole, *etc.* The presence of sulphuretted and cyanide compounds as well as ammonia compounds creates a risk of polluting the water by which the storage is sealed; this could extend to the Paris drinking water supply although, in the Beynes area, there is absolutely no contact between the gas storage seal water and the Paris drinking supply. Purification is done by means of iron oxide. (*b*) During withdrawal, the gas is purified from the hydrogen sulphide generated by micro-organisms in the structure. This is done in the same apparatus as that already mentioned, after changing the active masses. (In fact, the injection and withdrawal periods are not the same.) The removal of iron and/or nickel-carbon monoxide compounds formed in the structure, and whose presence even in very small quantities would extinguish pilot flames, is carried out on activated charcoal and the process is now running smoothly.

The Beynes storage equipment has resolved the problems of peak demand in the Paris area without the need for costly peak-shaving plant.

(3) Vernon

The Vernon gas storage in the Seine Valley, 50 miles south of Paris, is actually at the end of the prospecting stage. Part of the structure, which is very flat and 1,300 ft deep, is under the Seine. Whilst it has good cover, the storage reservoir itself is somewhat heterogeneous and composed of three layers of clayey sand with two possible reservoirs of 20,000 to 25,000 mill. cu. ft each. Pressure is fairly high at 800 lb/sq. in. The final objective at Vernon is an injection capacity of 90 mill. cu. ft/day and a withdrawal capacity of 140 mill. to 180 mill. cu. ft/day. The equipping of Vernon will not be continued unless important new resources of natural gas are discovered.

Prospecting is also being carried out elsewhere in France —in Bresse, Central France, and north of Paris; and the search for underground storage for liquefied petroleum gases continues in Provence.

VI THE SAHARAN DISCOVERIES

The year 1956 was very important for France because of the discoveries of hydrocarbon deposits in the Sahara.

Edjeleh and Hassi-Messaoud are oilfields whose associated gas (more than 7 mill. cu. ft/ton in the case of Hassi-Messaoud) will be re-pressurized into the deposit.

Hassi-R'Mel, with recoverable reserves of about 35 bill. cu. ft of sulphur-free gas, and approximately 12·5 lb/mill. cu. ft of condensable products, is, without doubt, the most important accumulation of natural gas in the world. This field is situated south of Algiers and about 280 miles from the coast; the gas-bearing structure is between 7,500 and 8,000 ft deep. At present, a 24 in. diameter pipeline connects the field with Arzew, near Mostaganem; a transverse line (Oran to Algiers) is shortly to be put into service. It is certain that the production of a field of this importance cannot be absorbed by Algeria alone, and the supplying of this gas to Europe is being studied.

An initial solution would be to liquefy the gas, at −260°F, in a coastal plant, and to transport the product in methane tankers to European ports. (The British gas industry having been the first to import liquid methane, by the *Methane Pioneer*, from across the Atlantic, I shall not discuss the great advantages of adaptability that this technique offers, nor its drawbacks, in particular the high costs of transport.)

France is studying plans for constructing methane tankers of 9,000 tons deadweight, and it is not impossible that in, say, three years time, Saharan methane may be liquefied in Arzew, shipped across the Mediterranean (to Le Havre, for instance) in quantities equivalent to 18,000 mill. cu. ft/year of gas.

The price of gas transported in this way has not yet been finally decided. An estimate, made by the Working Party on Gas of the European Economic Commission, Geneva, states the price of Saharan gas delivered to Channel ports and regasified as being of the order of 5·5*d*. to 6*d*./therm, on the assumption that the price of gas to the liquefying plant is of the order of 1·7*d*/therm. I am unable to confirm or question the merits of the assumed basic price of this gas, but the transportation price (3·8*d*. to 4·2*d*./therm) seems to tie in well with calculations made by specialists in Gaz de France.

The transportation possibilities of a pipeline across the Mediterranean is also being studied. Several routes suggest themselves: one through Tunisia, Sicily and Italy; a second through Morocco and Gibraltar. A third route, direct across the sea, from Mostaganem to Carthagena, is under particular study by Gaz de France, for, if technically feasible, it would seem to be the most satisfactory since it would reduce the total distance from Hassi-R'Mel to Northern Europe (North-East France—Belgium—the Ruhr), which would no doubt be an area of high consumption, to 1,750 miles.

During the summer of 1959, a hydrographic survey was made on the Mostaganem to Carthagena run (120 miles). The terrain was very favourable and absolutely flat, but descending to depths of 9,000 ft.

The pipelaying methods may now be considered to be ready, and it seems that only minor, technical problems inherent in all work done on the high seas remain to be solved. I am of opinion that the sea crossing by this route may be anticipated with optimism in the case of an initial, 36 in. diameter pipeline with a potential capacity of some 1,100 mill. cu. ft/day (350,000 mill. cu. ft/annum) at a service pressure of 1,000 lb/sq. in, the sea crossing being through several 12 in. diameter pipes at a pressure of 3,000 to 4,000 lb/sq. in. Cost of transportation by this means from the Algerian coast to Northern Europe of large quantities of the order mentioned would undoubtedly be less than by methane tankers, perhaps of the order of 1·7*d*./therm. Five or six years would seem to be necessary to carry out this scheme.

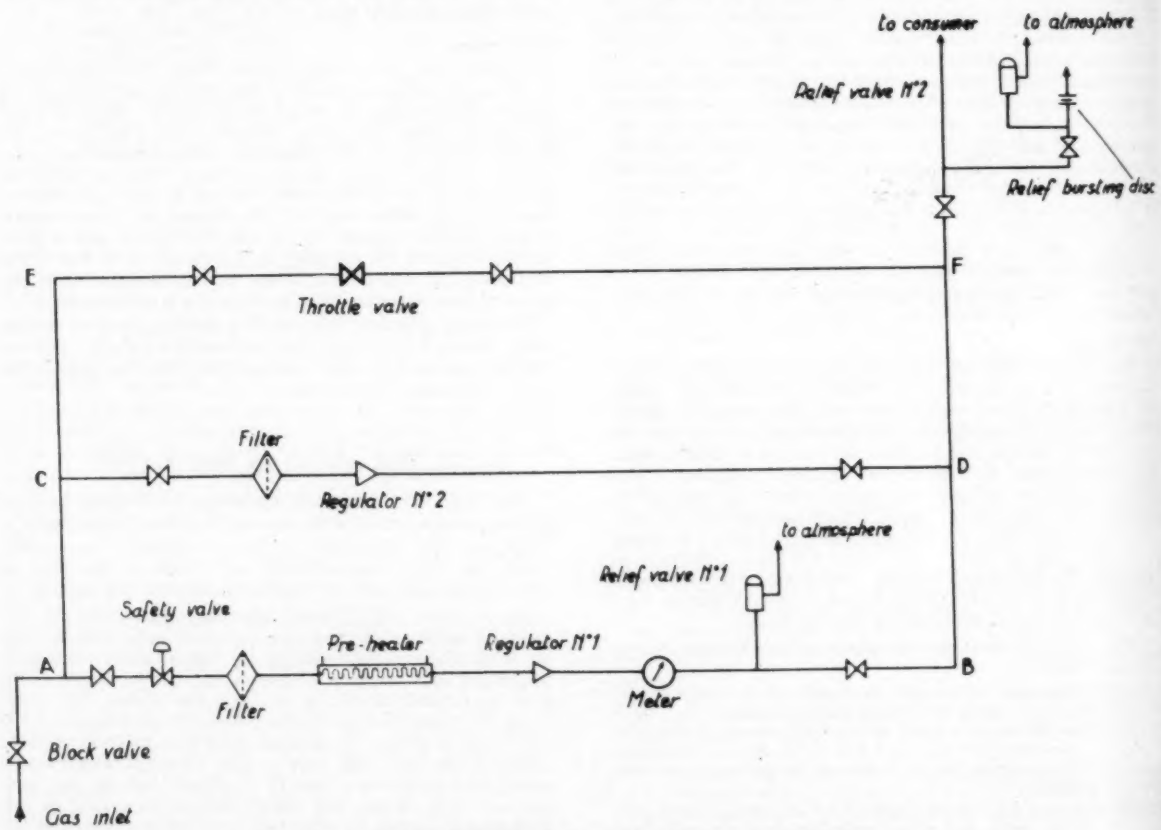

FIGURE 3.—*Diagrammatic Layout for the City-gate Station.*

VII EUROPEAN DISTRIBUTION OF SAHARAN GAS

The most favourable pipe run on the Continent of Europe for Saharan gas seems to me to be the eastern coast of Spain, with Barcelona as a supply region; then the Mediterranean coast of France (with a branch to Marseilles) and up the Rhône Valley to link with the Lacq system at Lyons. The continuation run would be towards Northern France, with possible branches towards Alsace, Switzerland, Southern Germany, the Paris region and Lorraine. Then through Belgium to the Ruhr; on this run, it would be possible to extend to the English Channel and Great Britain, with a channel crossing in all probability far less difficult than that of the Mediterranean.

Such a pipeline (36 in.) seems to me to be the minimum that might ensure a worth while transport price; in my opinion, the placing of 1,100 mill. cu. ft/day of Saharan gas on the Continent of Europe is highly possible.

I have no precise data related to the supply of such gas to countries other than France, but a recent study carried out in Gaz de France leads me to believe that, at price levels comparable with those for Lacq gas, the French market could consume as much as 600 mill. cu. ft/day of Saharan gas when such a distribution system as I have suggested might be put into service (say, towards 1968), as well as gas from Lacq and coke oven gas from the mining and steel industries. This does not include what Electricité de France might consume in its thermal works, nor what the metallurgical industry might use in blast furnaces and which, in my opinion, might amount to 200 mill. cu. ft/day each for Electricité de France and the metallurgical industry. Thus almost the whole capacity of the pipeline first planned would be absorbed.

TABLE 6.—*Development Prospects for the Whole of the Gas Industry for the Sale of Gas in France up to 1975, in the event of Saharan Gas becoming Available.*

Gas Sales (Mill. therms)	1960 (Provisional)	1965 (Expected)	1968 (Prospective)	1975 (Prospective)
1	2	3	4	5
Domestic, commercial and various other uses ..	535	730	1,190	1,525
Industrial use*	917	1,370	2,500	3,500
Total	1,425	2,100	3,690	5,025
Percentage of total consumption of fuel :				
Domestic, commercial and various other uses ..	7	8	9	12
Industrial use	13	17	24	26

* Excluding electricity production and blast furnaces.

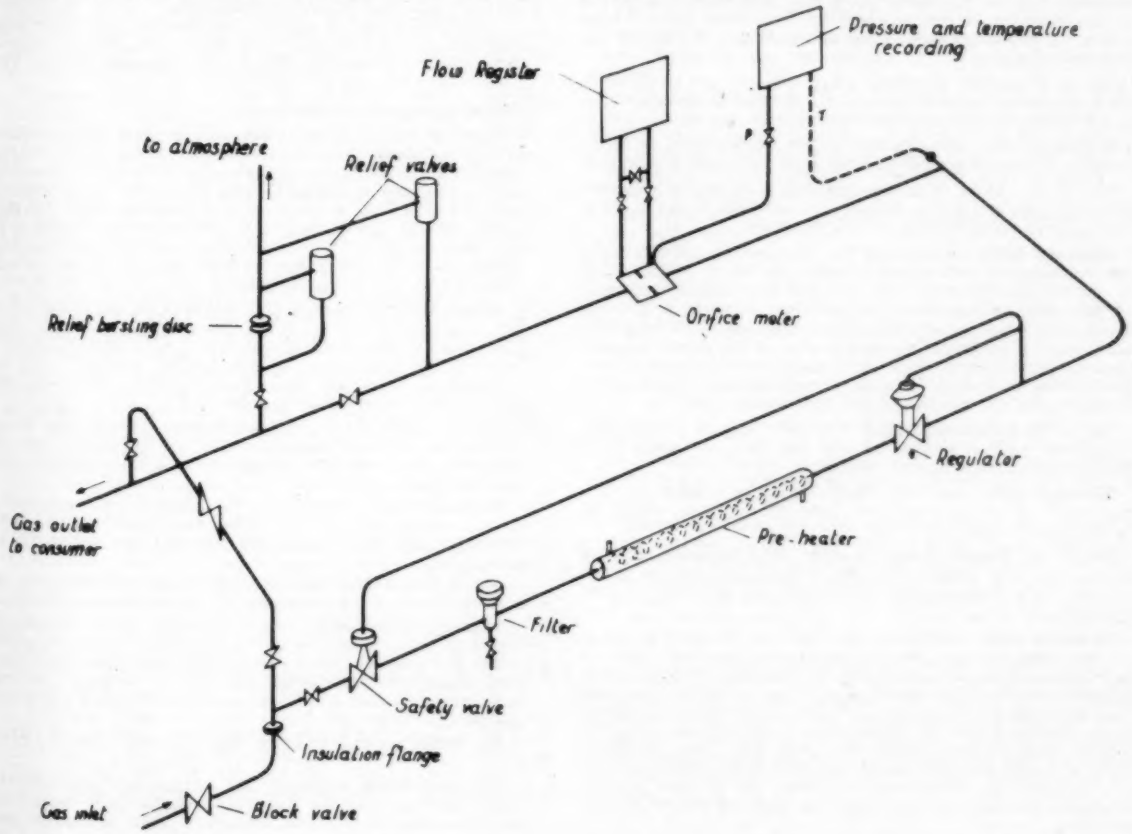

FIGURE 4.—*Diagrammatic Layout for a Delivery Station to an Industrial Consumer.*

This estimate might seem ambitious, but would appear to be admissible when compared with Tables 2 and 3, if Saharan gas should be available towards 1965-66.

The prospects are shown in Table 6.

Compared with the U.S.A., where gas supplies more than 50 per cent of the thermal energy requirements of the industrial sector, the 26 per cent indicated in Table 6 is not unduly optimistic.

These are the figures considered by the Planning Commission in relation to the prospects for the gas industry for the period 1965 to 1975, but I incline to the view that in the industrial field in 1975 it might be possible to reach 3,900 mill. therms, that is, 29 per cent of the total requirement, the remainder to be met by solid fuel as to 20 per cent (50 per cent in 1960) and by petroleum products as to, in round figures, 50 per cent (37 per cent in 1960).

It will be seen that the French gas industry, which at the end of the Second World War was considered to be "at death's door", is now well on its feet as a result of its enormous modernization of a highly compromised situation, and that resources of natural gas already acquired or in prospect open up such vast possibilites of development n the next 15 years as to fill all French gas technicians and salesmen with confidence.

DISCUSSIONS

The following discussions on Monsieur Odier's paper took place:—

London and Southern and Eastern Sections

Dr. A. E. Haffner (Southampton) said he was very interested in the underground storage of gas. For conventional types of town gas, carbon monoxide and hydrogen cyanide had to be removed. Useful information had been obtained from France on the change of calorific value on storage.

Mr. C. D. Shann (London) asked whether it was necessary to preheat the gas when reduced in pressure for city consumption.

Monsieur Odier said that this was not necessary during the summer. At the beginning, there had been some trouble due to the formation of methane hydrates from water when the gas was at a low temperature, but this had been solved by the injection of glycol.

Mr. S. F. Francis (London) asked why the gas at the wellhead was not expanded through the turbines to generate electricity and so make use of the reduction in pressure.

Monsieur Odier said this had been examined, but up to the moment it had not been considered as an economic proposition.

Mr. K. C. Mead (London) enquired how the change-over from conventional gas to natural gas had been achieved, bearing in mind the difference in calorific value.

Monsieur Odier replied that the difference in calorific value was considerable and originally was from 400 to 470 B.t.u/cu. ft. In the process of change-over, they had supplied propane/air mixture at about 600 B.t.u. and then propane/air at 1,100 B.t.u., which was a substitute for natural gas. In the future they intended to supply all natural gas. It had been necessary to make alterations to some appliances and to change others. The normal method of effecting the changeover was to carry it out in districts of about 5,000 consumers.

Mr. D. B. Parkinson, M.B.E. (Watford) said he noticed that consumers were dependent on one gas line, and asked what provision was made against failure.

Monsieur Odier said that repairs could be carried out in a maximum of about 8 hr, and most of the work could be carried out at night.

Mr. W. F. Parnell (London) asked what reduction in price of the gas was made since the natural gas was so much cheaper, and whether there had been any increase in consumption.

Monsieur Odier said that tariffs had been cut down by 20 to 25 per cent and that the original tariffs were not high by British standards. This reduction in price had resulted in considerable increases in consumption, which in some cases had been as much as 20 per cent. It was anticipated that output might double in two to three years. Natural gas was now looked upon as being competitive with oil. New buildings, such as hospitals, were being equipped with natural gas for all purposes. In the South of France, the increase in consumption had been greatest, being as much as 40 per cent in one area.

Dr. A. E. Haffner, in proposing a vote of thanks, said the paper was of great interest and a fascinating subject. His envy of the French gas industry in its fortune in discovering such a large source of natural gas had changed to admiration of the engineering skill shown in its development, which had been most stimulating. In addition, the willingness of Gaz de France to give details and information had been greatly appreciated.

North of England Section

Unfortunately, the time available for discussion was restricted and it was possible for only very few members to participate.

Mr. K. E. Brown (Senior Vice-Chairman), in proposing a vote of thanks, warmly congratulated Monsieur Odier not only on his very interesting and informative lecture, but also on the very able way he had presented it.

Appreciation and thanks for the facilities and refreshments provided by the Northern Gas Board and Mr. W. Sutcliffe, B.Sc., were expressed by **Mr. K. W. Francombe** (Junior Vice-Chairman) on behalf of members.

Manchester and District Section

Mr. G. E. Currier, O.B.E. (Honorary Secretary, The Institution of Gas Engineers) congratulated Monsieur Odier on his excellent account of the developments of the gas industry in France. He was particularly interested in the wonderful achievements of the technicians in overcoming the problems and difficulties caused by the high sulphur and carbon dioxide content of the gas finds at Lacq. He mentioned also that the experience gained in the *Methane Pioneer* experiment might be of some advantage to the French engineers.

Monsieur Odier said that from the start the gas found at Lacq was very difficult to deal with. Before any exploitation of the deposit could take place, a steel had to be produced capable of resisting the acid attack of the sulphur content. This was achieved in 1955, and from then onwards there was rapid development on a commercial basis.

Mr. J. Castle (Liverpool) asked what happened to the gas transmitted from the Lacq system to the Paris area, where gas from the coke ovens grid system and at a lower calorific value was apparently still used.

Monsieur Odier replied that the Lacq gas was reformed at Paris to a calorific value of 470. The Paris area was rather unusual in that 40 per cent of the country's load was used in this area.

Mr. F. Litler (Manchester) enquired why reforming was still carried out when there were such large reserves of natural gas.

Monsieur Odier replied that in Paris the use of reformed gas would go on for a long time; it was employed to a considerable extent for peak shaving. Eventually, there would be a complete change-over to natural gas. In two to three years, the large cities of Lyons and Nantes would be supplied with natural gas only.

Mr. Litler wanted to know also how the change-over was made.

Monsieur Odier answered that burners and injectors were first converted, and the distribution system was divided into sectors so that about 5,000 consumers could be changed overnight, one sector following the other.

Mr. R. J. Bradshaw (St. Helens) suggested that because of

the higher pressures used, smaller service and carcassing pipes could be used.

Monsieur Odier agreed.

Mr. F. C. Barker (Leeds) questioned the speaker on the availability of supplies at Lacq, and asked also where odorization took place.

Monsieur Odier replied that reserves at Lacq were estimated to last for 30 years. Odorization took place at the city gates and not on the transmission line.

Mr. N. C. Sturrock (Harrogate) thanked Monsieur Odier for his excellent address, and the members present showed their appreciation most warmly.

Wales and Monmouthshire Section

Mr. W. T. Hird, M.B.E. (Cardiff) stated that at the Institution's 96th Annual General Meeting, at Llandudno, in 1959, a paper was given by Monsieur Fouchier and Monsieur Vicart dealing with the development of natural gas at Lacq. They had heard from Monsieur Odier the impact of that development on Gaz de France. There were many points he would have liked to raise, but he proposed to deal with one question only. Monsieur Odier had said that in some towns, such as Nantes, natural gas was now distributed to consumers, while in other towns, such as Lyons, the natural gas was reformed before distribution. He said he would be most grateful to know the reasons that resulted in the decision to distribute straight natural gas in some places and to reform it in others. He would also be interested to know in what type of plant natural gas was reformed. In conclusion, he congratulated Monsieur Odier on his excellent command of English and for the trouble he had taken to give all figures in English instead of metric units. This was, indeed, a most courteous and helpful refinement and one that he knew that all appreciated. He added that from his past experience with Monsieur Odier it was very typical of him.

Monsieur Odier stated that the decision as to whether straight natural gas or reformed natural gas should be distributed was made in the light of availability of the skilled labour necessary to convert consumers' appliances. Gaz de France realized that the amount of work involved was such that it would not be possible for all towns receiving natural gas to be converted as quickly as supplies of natural gas became available in those towns. It was, therefore, decided that the programme would be prepared allowing for the maximum conversion to straight natural gas, and for that reason it would be necessary for some of the very large towns, such as Lyons, which had available suitable plant for reforming gas, to distribute reformed gas and for the skilled labour force available to convert, in the first place, as many of the smaller towns, such as Nantes, as possible. It was hoped that in the future it would be possible to convert the towns, such as Lyons. In Paris, the position was different, since the supply of natural gas was not sufficient to become the sole supply, and large supplies of coke oven gas, made in plants belonging to Gaz de France and also transported from Lorraine, would continue to be used. It was, therefore, necessary for the natural gas to be reformed so as to be interchangeable with existing supplies. The plant used for reforming the natural gas are generally of the "Onia-Gegi" type.

Mr. J. R. Marshall (Vice-Chairman, Southern Section, The Coke Oven Managers' Association) asked Monsieur Odier how long the estimated reserves of gas would last, and if there was any possibility of the present calorific value of the gas changing during the life of the underground reserves. He had recently read of the work carried out by the Northern Gas Board on using an underground cavern for gas storage, and would like details if similar investigations had been undertaken by Gaz de France.

Monsieur Odier, in reply, stated the estimated reserves of the Lacq gasfield, when fully developed at 7·5 bill. cu. ft/year, would not be less than 30 years, and there was no reason to anticipate that the gas characteristics would change over this period. No work had been done in respect of underground caverns, but he amplified the details given in his paper on the exploitation of underground existing storage sites and field reconnaisance work in proving additional sites.

Mr. S. L. Wright (Cardiff) proposed a very hearty vote of thanks to Monsieur Odier for his most interesting and informative paper, and he was certain all members were more than impressed, not only by Monsieur Odier's command of the English language, but his ready ease in dealing with equivalents of metric weights and measurement. The cine-film of the Lacq installation and slides of all aspects of the nation-wide gas transmission system left no one in doubt of the immense amount of research and development work that had been carried out by Gaz de France.

Mr. J. R. Marshall, in seconding the vote of thanks, expressed, on behalf of his Association, pleasure in participating in the joint meeting, and to Monsieur Odier for his wealth of information of the horizons opening up before the gas industry.

All present enthusiastically supported the vote of thanks.

Midland Section

Mr. S. K. Hawthorn (Chairman; Birmingham) said he was sure the audience were filled with envy at the resources available to their French friends, but there were a great number of distribution problems in which they were interested.

Replying to **Mr. E. W. Pickering** (Derby), **Monsieur Odier** said that they had tried not to exceed a velocity of 40 to 50 ft/sec in the mains, though it might rise to 80 ft/sec. Something like 70 mill. cu. ft of natural gas was received in Paris. This was reformed and mixed with oven gas from Lorraine. The cost of change-over from manufactured to natural gas in, say, Lyons was around £20/consumer.

Mr. R. W. Nelson (Birmingham) asked about the rate and cost of mainlaying, and the use of "pigs" for cleaning the pipes.

Monsieur Odier said that mains were laid at about 2 miles/day; 12 in. mainlaying cost something like £10,000/km. The "pigs" were used regularly. Bends were in the region of a radius of 50 diameters, but the "pig" was not absolutely rigid and could bend slightly. They were quite satisfied with metering through orifice plates.

Replying to **Mr. F. L. Atkin** (Birmingham), **Monsieur Odier** said that electric welding was used (not fusion welding) in the construction of the pipes. Testing of the joints was by X-ray. Testing of completed sections was hydraulic at a pressure 10 per cent above working pressure, maintained for 10 days. The use of gas heaters prevented trouble from icing of regulators.

Mr. W. R. Branson (Deputy Chairman, West Midlands Gas Board) remarked that the most important part of any vast project, such as that described by Monsieur Odier, must be the planning of distribution and the estimation of sales. He thought that Monsieur Odier's forecast of an increase in domestic consumption of no more than 7 to 8 per cent might be a little pessimistic. He would have thought that one way of arriving at reasonable figures would be to base them on large consumers only and take the smaller consumers into account at a later date.

Monsieur Odier said that the increases of 20 to 30 per cent were envisaged for the next two to three years. Space heating load was increasing at about 5 per cent per year. All the big new housing schemes were providing for gas central heating and hot water supplies, which had helped in their estimations. It was expected that by 1970 the new tariffs now existing in South West France would be extended to most of the country.

Mr. F. Harvey (Walsall; Vice-Chairman), proposing a vote of thanks, said that never had this duty given him greater pleasure than on this occasion, both because of the interesting subject matter and of the personality of the speaker and the quality of his presentation of the paper. One fact that emerged from the meeting was that the French had shown tremendous vision in taking advantage of the opportunities available to them.

In this Issue...

L. Barker was educated at Morley Grammar School and at the University of Leeds. He took an honours degree in Chemistry and since then he has been engaged on different research problems at the University. As a result of post-graduate research in the Fuel Department, he obtained a Ph.D. degree for an investigation into the catalytic production of carbon black. Subsequently, in the Textile Department, he was engaged in the development of oils for use in the wool industry. Since 1946, he has been a member of the research team that is now governed by the Joint Research Committee of The Gas Council and the University of Leeds, and has been concerned in the catalytic hydrogenation of organic sulphur compounds in town gas, and later in the composition of gas works ammoniacal liquors. The Gas Council's *Research Communication GC*70 is the fourth of a series, presented to The Institution of Gas Engineers, in which he has been associated with other colleagues.

N. W. Hollingworth was educated at Bolton County Grammar School and took a degree in Chemistry at the University of Leeds in 1951. He then undertook research for the Joint Research Committee of The Gas Council and the University of Leeds, studying problems concerned with the composition of ammoniacal liquors. After a period of National Service, he returned to the organization to continue the investigation and has been responsible for developments in the chromatographic analysis of liquors.

J. K. Kilham was educated at Archbishop Holgate's Grammar School, York, and the University of Leeds, where he graduated with first-class honours in Chemistry in 1942. Research on reaction kinetics led to the degree of Ph.D. in 1944. He held the Third Arthur Duckham Fellowship from 1945 to 1947, during which time he studied the mechanism of energy transfer from flame gases to solids in the Fuel Department of the University of Leeds. Since 1947, he has been employed by the Joint Research Committee of The Gas Council and the University of Leeds. He is the author of several papers on heat transfer from flames.

E. G. Jackson was educated at Aireborough Grammar School, Aireborough, and the University of Leeds, where he obtained a first-class honours degree in Gas Engineering in 1949. Research on heat transfer from flames led to the award of a Ph.D. degree in 1954. Since 1949, he has been employed by the Joint Research Committee of The Gas Council and the University of Leeds. Before studying tunnel burners, he investigated the structure of flames, using flow visualization techniques, and heat transfer from flames to solids.

T. J. B. Smith was educated at Burton-upon-Trent Grammar School and the University of Leeds. where he graduated with honours in Electrical Engineering in 1957. Since then, as a research assistant to the Joint Research Committee of The Gas Council and the University of Leeds, he has been engaged on a programme of research into the basic sources of noise arising from combustion processes.

Roger Odier, Ingénieur des Arts et Manufactures of the Ecole Centrale in Paris, entered the gas industry in 1933, with the Compagnies Réunies de Gaz et d'Électricité. From 1933 to 1945, he was Engineer of the works at Rheims and at Angers. After a period with Electricité de France, from 1945 to 1949, he became Commercial Manager of the Eastern Division of Gaz de France. At the same time, he acted as Secretary of two missions organized by O.E.E.C. dealing with long-distance transmission of gas in France and Italy and in the U.S.A. respectively. At the end of 1956, he joined the commercial management of Gaz de France, subsequently called the Directorate of Economic and Commercial Services, and has been, since 1958, the Director of its Research Department.

L. Barker

N. W. Hollingworth

J. K. Kilham

E. G. Jackson

T. J. B. Smith

R. Odier

Proceedings of Council

The following matters of general interest were among those dealt with by the Council:—

COUNCIL MEETING, 28th FEBRUARY, 1961

It was resolved to nominate the following for election by ballot of the Corporate Members, as officers of the Institution for the year 1961-62:—

President:	Mr. T. C. Battersby, M.B.E.
Honorary Secretary:	Mr. G. E. Currier, O.B.E.
Auditors:	Sir Harold Smith, K.B.E., D.L. Mr. P. D. Davey, F.C.A.

Consideration was given to the names of persons to be nominated by the Council for election as Honorary Members.

The accounts of the various Institution funds for the year ended 31st December, 1960, were considered and, subject to audit, approved for presentation at the 98th Annual General Meeting. The budgets of income and expenditure for 1961 were also considered and approved.

Reports were received of the following meetings of Committees of the Institution:—

(1) PUBLICATIONS COMMITTEE, on 11th January

(*a*) The Committee had considered critically the first issue of the *Journal* and had agreed improvements for future issues.

(*b*) It had been agreed to include, as a regular feature of the *Journal*, a monthly page of abstracts and notes from foreign periodicals, and Dr. W. T. K. Braunholtz had agreed to undertake to prepare these.

(2) COMMITTEE ON UNACCOUNTED-FOR GAS, on 22nd February

Subjects discussed had included the measurement of temperature and pressure of gas in domestic meters, leakage from gasholders, *in-situ* tests on industrial meters, registration of gas made, and leakage from fractured mains and services.

Reports were made of addresses presented by Monsieur R. Odier (Gaz de France) at meetings of District Sections in Birmingham, Cardiff (at a joint meeting with The Coke Oven Managers' Association), London, Manchester and Newcastle-upon-Tyne. These meetings had been most successful.

It was reported that meetings of the Council of the International Gas Union would be held in London on 20th to 22nd March, 1961. In addition to business sessions, the programme would include a reception at Lancaster House by H.M. Government, a luncheon given by The Institution of Gas Engineers, a dinner given by The Gas Council, and a visit to the "Ideal Home" Exhibition.

It was reported that Dr. R. H. Griffith, D.Phil., B.A., had resigned from the British National Committee for Chemistry, of the Royal Society, on which he had represented The Institution of Gas Engineers, and that Mr. G. U. Hopton, B.A., B.Sc. (Director, London Research Station), had accepted the invitation of the Council to serve in his place.

The following changes in the representation of the Institution on technical committees of the British Standards Institution were approved:—

(*a*) The resignation, upon retirement, of Mr. W. Kay as a representative of the Institution on Technical Committee MEE/10—Engineering Drawing Office Practice.

Mr. J. Verity continued to represent the Institution on this Committee.

(*b*) The resignation of Mr. J. Sharp Smith as representative of the Institution on Technical Committee INE/4/1—Optical Pyrometers.

It was resolved to invite Mr. R. Kynch to serve as representative of the Institution, as well as of The Gas Council, on this Committee.

Institution Register

Transfers

To Membership:

Bryce, William John Griffiths	Walsall
Cormack, John David	Sutton Coldfield
Perriss, Cecil Edward	West Croydon
Topley, Douglas Henry, B.Sc.(Eng.)	London

Admissions to Studentship

Bracken, Paul Alexander	Winsford
Calvert, Robert	Anglesey
Croft, Michael Brian	Birmingham
Davies, Christopher Lyndhurst	Kilgetty
Fleming, Kevin Joseph	Sheffield
Harris, David	Sheffield
Hewitt, John Charles	Newport
Hull, Peter Leslie	Stoke-on-Trent
John, David	Cardiff
Llewellyn, David James	St. Athan
Pearce, Malcolm Francis	Whitchurch
Perkins, Ronald James	Derby
Street, Michael Colin	Grantham
Watson, Malcolm Norgrave	Bradford

Deaths

The Council regrets to announce the death of the following Member of the Institution:—

Robertshaw, Percy (Ovenden) M.1951; died 5th February, 1961.

News from the Gas Industry Overseas

The full text of articles abstracted below may be consulted in the Library of the Institution.

Gas in Argentina

J. des Industries du Gaz, 1961, Feb. 57-60

The history of the gas industry in Argentina falls into three stages. The first stage commenced in 1856 with the formation of a company the principal activity of which was the sale of by-products from the carbonization of coal, with gas as a residual used for public lighting. The gas industry as a public service was nationalized in 1945, by which time the total number of consumers in Buenos Aires and its suburbs, had only attained 200,000. Gas manufacture was developed and, simultaneously, the use of natural gas was extended. By 1950, a long-distance transmission pipeline, some 1,000 miles long, brought natural gas from the south to Buenos Aires and served to supply other parts of the country. When the original deposits of natural gas showed signs of exhaustion, new deposits were found and new pipelines laid. It is estimated that, by 1964, some 800 mill. ft³/day of natural gas will be transported by three main pipelines, and the value of this gas will be equivalent to about 40 per cent of the total annual imports of fuels.

The increasing use of gas is shown by the growing number of consumers, *viz:*—

	Consumers
1945	200,000
1950	327,000
1955	522,000
1957	600,000
1959	725,000
1960	1,080,000

The article includes a map showing the gas and oil deposits, refineries and gas pipelines throughout Argentina.

Experiences with L.P.G./Air Mixing Plants

G. Gaikhorst. *Monatsbulletin*, 1961, Feb., 29-36

The paper describes experiences with the supply of propane/air mixtures as town gas in Holland. Such mixtures have the advantage over undiluted L.P.G. of reducing distribution losses and overcracking or reforming of retaining 100 per cent efficiency. Oxidation of distribution pipes is avoided, in spite of a concentration in the gas of about 21 per cent O_2, by preventing condensation of moisture on the metal. The drying out of jointing materials and consequent leakages due to the dry gas is avoided by injecting a small quantity of oil into the gas stream. In Holland, propane is stored exclusively above ground. Mixing with air is effected either by injection or by volumetric proportioning. Since propane/air is heavier than air, precautions must be taken to avoid its accumulation in cellars and basements by (*a*) installing meters above ground level, and (*b*) preventing gas seeping into the house, from exterior leaks, through holes in the wall. Details are given of the conversion of various types of appliances from coal gas to propane/air, and the paper is illustrated throughout with a number of drawings.

Slagging Fixed-bed Pressure-gasification Plant

Walter H. Oppelt. *Gas Age*, 1961, **127**, 34-35, 60

Because of rising gas demand in the U.S.A., it is probable that, in the future, the supply of natural gas will have to be augmented by total gasification of coal. The Lurgi process is particularly suited to the gasification of lignite, large quantities of which occur in North Dakota. In order to increase the gasifier efficiency and capacity, the Grand Forks Lignite Research Laboratory of the Federal Bureau of Mines has developed a slagging-type fixed-bed pressure gasifier in which the ash is discharged at temperatures above its fusion-point. Operating under slagging conditions reduces steam and cooling water requirements and volume of water to be processed, while increasing steam usage, over-all thermal efficiency of the process and capacity of the gasification unit.

The gasification pilot plant is described, and its design illustrated by a drawing and photograph. The generator is of 15¼ in. i.d., and the fuel bed area is 1¼ ft². Its total height, including coal and slag locks, is 39½ ft, and it is designed to withstand an internal pressure of 700 lb/in². The liquid slag, at about 2,600°F, is discharged into a water-filled trough where it is quenched and granulated. After 23 runs at a test pressure of 80 lb/in² and with low-temperature coke as fuel, it is concluded that gasification under slagging conditions is feasible and improves the efficiency of operation.

C.G. and E. Digs Again for Second Huge Storage Cavern

A.G.A. Monthly, 1961, Feb., 16-17, 31

The Cincinnati Gas and Electric Company is digging a second huge cavern in the limestone formations of Kentucky for the storage of liquid propane 450 ft underground. A gas processing plant will also be constructed about 2½ miles from the cavern, with an 8 in. pipeline conecting the two through which the liquid propane will be transported. The cavern and plant will be used to supplement the gas supply in cold weather.

The new cavern will be of multi-room design, about 180 ft by 330 ft with 30 ft ceilings. Tunnels connecting the rooms will be 30 ft by 30 ft, and supporting pillars will measure 40 ft by 40 ft. The storage capacity will be 7½ mill. gal of liquid propane.

The mining engineering technique, which is described, is of interest. To begin with, a hole is drilled to the desired 450 ft depth and lined with steel casing. Miners descend, set explosive charges, re-descend and remove the loosened limestone by hand. This is repeated many times until the hole is large enough to accommodate more miners and, ultimately, mobile shovel loaders and earth-moving equipment, which is disassembled before being lowered and reassembled at the shaft bottom.

When the cavern is completed, capped and tested, it will be filled with liquid propane which will then, in cold weather, be pumped to the processing plant and there gasified.

Gas Helps City Clean Up its Air

Morton Sterling. *A.G.A. Monthly*, 1961, Feb., 21-22, 31-32

An account is given of a joint investigation by the Detroit Bureau of Air Pollution Control, the local gas undertaking, and gas appliance manufacturers to develop domestic gas-fired incinerators of acceptable performance from the point of view of air pollution. The previous incinerators were of the so-called "low-input" (or dehydrating) and "high-input" types. Complaints in Detroit over several years indicated that about 75 per cent related to smoke and odour resulting from the "low-input" incinerators, due to the smouldering condition in the waste bed. The "high-input" unit often caused more dense smoke emission for a shorter time.

The newly developed domestic incinerators follow the established pattern of commercial incinerators in which the primary combustion products flow into a secondary chamber where they pass through an enveloping flame. This dual-chamber feature has been achieved with little or no increase in external size and with no significant decrease in holding capacity. The burner discharges about one-third of its thermal output into the primary chamber and two-thirds directly into the secondary chamber, a single venturi and control system feeding gas to the dual-purpose burner.

In all cases, duplicate tests for each charge were run for smoke, odour and fly-ash evolution. The results have shown that there is a substantial reduction in smoke liberation, particulate emission and odour emission from the new incinerators, but the attainment of this improved performance has involved significant increases in the total auxiliary fuel requirements per pound of waste consumed.

Automation and Safety in the Gas Industry

F. Schuster. *Gaswärme*, 1961, Jan., 63-68

After discussing the meaning and purposes of automation, the Author rejects the possibility of a thinking machine. From the point of view of safety, fuel gases have the drawback of their combustibilty (leading in certain conditions to explosion) and the toxicity of mixtures containing carbon monoxide. To counter these drawbacks, it is necessary to prevent the escape of unburned gas at gas appliances. Various devices have been developed to ensure safety from this eventuality, in particular bi-metallic controls, thermo-electric controls and electronic controls. The Author shows, by means of drawings, the stages in the development of methods of burner ignition from manual control of every operation up to completely automatic control. Practical examples are given of these types of control and of multi-stage automatic safety devices for igniting gas at a burner and for turning off the supply in the event of flame failure. All these types of safety devices are theoretically applicable to all types of fuel, but gas is particularly amenable to them by reason of its fluidity, its freedom from solid particles and its complete miscibility with combustion air.

District Sections and Affiliated Associations

(a) Notes of Meetings

DISTRICT SECTION

London and Southern Section

A large number of members attended the meeting held on Tuesday, 21st February, 1961, when a paper, entitled "The Production and Marketing of 'Cleanglow'", was presented by Mr. C. C. Cunnold (Group Engineer) and Mr. D. G. Rose (Coke Manager), North Thames Gas Board. The Section was honoured by the presence of Dr. J. Burns, G.M. (Deputy Chairman, North Thames Gas Board). Before the presentation of the paper, Mr. J. A. Hepworth (Chairman of the Section) congratulated eight successful candidates in the examination for Associate Membership of the Institution, and presented certificates on behalf of the Institution. Mr. C. C. Cunnold then presented the section of the paper dealing with the production of "Cleanglow", followed by Mr. D. G. Rose on its marketing. An interesting discussion ensued.

A vote of thanks, proposed by Mr. A. H. Savill, was heartily accorded.

JUNIOR GAS ASSOCIATIONS

Midland Junior Gas Association

(*a*) The President (Mr. R. W. Nelson) was in the Chair, and 50 members were present at a meeting held in the Staff Mess Room, Birmingham, on Tuesday, 24th January, 1961.

The President announced with deep regret that, since the last meeting of the Association, Mr. W. E. Groves and Mr. A. E. Trinder, both of Birmingham, had died. At his request, all members stood in silence to respect their memory.

The President then introduced Mr. W. Jones, A.M.I.Gas E. (Divisional Distributing Engineer, North Staffs. Division, West Midlands Gas Board), who presented his paper, "The Distribution of Gas through Steel Pipes". This was followed by a discussion.

Mr. A. V. Wainwright proposed a vote of thanks.

(*b*) The President (Mr. R. W. Nelson) presided at a meeting held at Birmingham on Tuesday, 7th February, 1961, when 75 members attended. He welcomed Mr. D. J. O. Bath, a past President of the Midland Junior Gas Association.

The President announced with deep regret the death of Lt.-Col. F. J. Bywater, C.B.E., M.C., the first President of the Midland Junior Gas Association. After the President had paid tribute to Col. Bywater, members stood in silence in respect.

The Honorary Secretary (Mr. W. E. Dobson) announced that the Chairman of the Midland Section of The Institution of Gas Engineers had invited members of the Association to attend the Section's meeting at Birmingham on 3rd March.

The President then introduced Mr. A. Yates, M.I.Gas E. (Assistant Gas Engineer, Wales Gas Board) who presented a paper, "Notes on the American Gas Industry, 1960". A film, "More Gas for More People—Naturally", was shown; it described the reasons for the construction and application of an underground aquifer at Troy Grove, Northern Illinois, and was appreciated by all members present. A lively discussion was opened by Mr. W. E. Dobson, to which several members contributed.

A vote of thanks was proposed by the Senior Vice-President, Mr. A. V. Wainwright.

(c) At Birmingham on 21st February, 1961, the President (Mr. R. W. Nelson) presided over a meeting of 55 members.

Mr. K. Davis, M.I.Gas E., M.Inst.F. (Divisional Industrial Gas Officer, North Staffs. Division) and Mr. L. Walker, M.Inst.F., A.M.I.Mech.E. (Assistant Industrial Gas Officer), West Midlands Gas Board, presented a paper, "Design and Operation of Gasfired Multi-passage Kilns". Mr. S. Brockbank opened the discussion, to which a number of members contributed.

A vote of thanks was proposed by the Senior Vice-President (Mr. A. V. Wainwright).

Western Junior Gas Association

A meeting of the Association, held at Exeter on Saturday, 18th February, 1961, was attended by approximately 70 members and guests.

The meeting commenced with a visit to the Basin Gas Works, to see the final stages of the works reconstruction in progress. Items of major interest were the Appleby Frodingham desulphurizing plant and Power-Gas sulphuric acid plant, now in course of erection, and the recently completed primary flash distillate installation supplying P.F.D. to the carburetted water gas plant. Other plants installed since the Association's previous visit to Exeter included a butane/air plant and the aftercooler installation on the outlet of the gas compressors.

Following the works visit, members reassembled at the South Western Gas Board's new Service Centre at Eastgate, Exeter, for the presentation of Mr. D. D. Way's paper entitled "Some Aspects of Automatic Control on Holder Stations".

At the conclusion of the meeting, Mr. T. A. Nicholson (Taunton) proposed a vote of thanks to Mr. L. Baldwin (Works Engineer and Manager, Exeter) and his staff for the excellent arrangements made for the works visit, and to Mr. D. W. Baker (District Manager) for the arrangements made for the afternoon meeting.

(b) Abstracts and Discussions of Papers

Copies of the complete papers abstracted below are available for consultation or loan in the Library of the Institution.

DISTRICT SECTIONS

London and Southern Section

"The Production and Marketing of 'Cleanglow'", *by C. C. Cunnold, A.M.I.Gas E. (Group Engineer), and D. G. Rose, B.Sc., M.I.Gas E. (Coke Manager), North Thames Gas Board.*

Paper delivered in London on 21st February, 1961.

Tests carried out by the North Thames Gas Board in 1955 showed that it was possible to produce a highly reactive fuel by carbonizing low-rank coal in continuous vertical retorts. A feature of this process was a much faster flow of coal through the retort, compared with conventional carbonization.

Coal of suitable rank, ash content and swelling index was available in the East Midlands, although in limited quantities, and supplies could be conveniently taken by rail at certain of the Board's works with suitable carbonizing plant. At first, coals of double and treble grading only were carbonized, but, with changes in the industrial coal prices, it become economic to use a proportion of singles. The "Cleanglow" produced from singles was satisfactory although the proportion of nuts and breeze produced was higher than that associated with the larger coal.

As available supplies of coal increased, so it was possible to add to the number of stations producing "Cleanglow". The idiosyncrasies of plant were overcome by careful selection of coal and control of operations to ensure that "Cleanglow" of consistently high quality continued to be produced despite the increase in the number of manufacturing points. The successful production of "Cleanglow" depends on maintaining a high throughput while keeping combustion-chamber temperatures at their normal level. If anything, even closer control of carbonizing conditions is required than in traditional coal gas production.

The higher price commanded by "Cleanglow" makes it inadvisable to use this fuel either for producers or as a source of diluent gas for the control of calorific value. Normally, it is more economic to import cheaper grades of coke for these purposes.

A study of the cost of gas making by the "Cleanglow" process, compared with conventional carbonization, suggests that, despite the lower thermal yield of low-rank coal, there is a slight cost advantage in its use. If this is satisfactory, then certainly the public response to "Cleanglow" itself is even more so.

"Cleanglow" provides an interesting example of the interrelationship of ideas springing from engineering and commercial departments. It was introduced in 1956, the year in which the Clean Air Act was passed, and since then the new fuel's progress has matched that of clean air very closely. It would be wrong, however, to tie "Cleanglow" too closely to smoke control areas as such; its contribution to clean air has been more general.

"Cleanglow" led the way for a new approach to the marketing of all "gas coke", by which various types and grades have been separated and defined by name and price.

Discussion

Dr. J. Burns, G. M. (London) recalled the development of the manufacture of "Cleanglow", and said that in 1955 it was apparent that the slow development of a coal price structure would result in the price per therm of carbonizing coal increasing above that of coal used for other purposes, and that this would particularly affect the North Thames and South Eastern Area Gas Boards, which used Durham coal. This led to the idea that something might be done with other coals. Initially, an experimental trial was carried out on 50 tons of low-rank coal at Bow Common. The North Thames Gas Board then allowed full-scale carbonization of low-rank coal in order to establish the yields and carbonizing procedure. A batch of

500 tons was carbonized at Kensal Green. Dr. Burns took the opportunity of complimenting those concerned, from the stokers who man-handled the coal to the engineers who watched the results. The problem of marketing and price differential then arose and it was decided that the price differential had to be right from the beginning. The reaction to the production of "Cleanglow" by the National Coal Board was quite helpful, and Mr. T. C. Finlayson, C.B.E. (Woodall-Duckham Company Limited), from his experience, gave considerable assistance in the choice of suitable coals.

The National Coal Board later realized that "Cleanglow" was cutting into its own domestic sales, but eventually appreciated that it was good policy to supply the coal up to its availability. Dr. Burns finally complimented those responsible for marketing the "Cleanglow" who had faith in their belief that it would eventually be successful.

Mr. L. F. Garner (St. Albans) said that "Cleanglow" had been manufactured at St. Albans since September, 1960, and a new West vertical system was also now being used. He gave figures of the increased throughput of coal and make of gas, in which an ample supply of producer gas, sufficient to carbonize the coal adequately, had materially assisted. He said that details of the daily results obtained were telephoned to the Divisional Engineer and to the Coke Sales Manager, and, in consequence, any complaints were easily followed up. These were not many, but some complaints of flocculent ash had been received.

Mr. C. A. Deas (London) said the paper was of great topical interest and that the demand for smokeless fuel was increasing, particularly in the new towns. He emphasized, however, that it was necessary to maintain consistent good quality. He considered that in specifying the coal the shale content was particularly important as customers disliked paying money for pieces of stone remaining in their grates. He stressed the importance of the high rate of coal travel through the retorts, and said this applied also to the manufacture of "Gloco", which, he considered, was almost up to the standard of "Cleanglow". He had found in smoke control areas that consumers preferred to use the higher-priced fuels, and generally the demand for these exceeded production. He paid tribute to the North Thames Gas Board in getting the fuel recognized by the public. As a cloud on the horizon he wondered whether the supply of coal suitable for "Cleanglow" manufacture would be adequate, although he felt that this should be the case as large quantities were sold elsewhere for other purposes. He regretted also the general tendency for the reduction in the output of solid fuel and stressed that the economics of gas production from coal depended largely on the revenue obtained from the solid residue.

Mr. W. P. Smith (Leicester) complimented the Authors on a very informative paper and confirmed that increased throughput gave the maximum reactivity in coke. He had not found it possible at Nottingham to get as high a coal throughput as that quoted in the paper, and had found that continual supervision of coke extraction was very necessary. He asked whether the increase in throughput resulted in any increase in scurf formation, and also whether any special precautions were required to ensure adequate mixing of different types of coal. At Nottingham, this had been attempted by putting layers of the different coals in the top hopper by means of the coal shuttle.

Mr. F. Dawson (Lea Bridge) said the process of manufacturing "Cleanglow" had been very stimulating. On the practical side, the production of dust had created some problems and it was essential to quench the coke as soon as possible. The use of wetting agents with the water was useful, but these could only be used when the coke had first been cooled. He gave details of the methods of storage employed and also of the increase in output, which, however, had created considerable strain on the remainder of the plant. The quantity of producer fuel used had been found to be approximately the same per day as when "Gloco" was being produced, and he suggested that the transfer of heat to the coal was improved by the absence of the normal plastic layer.

Mr. Arnold Marsh, O.B.E. (London; Director of the Clean Air Movement) congratulated all concerned in the production of smokeless fuel, the demand for which, he felt, was only at its beginning. He considered the development of smokeless areas would accelerate, and he hoped the gas industry would redouble its efforts to produce such fuels as "Gloco", which, he felt, would be more likely to be made than "Cleanglow". There still existed much criticism of coke, usually partly due to its misuse by the consumer, but also partly due to its poor quality. Adverse publicity in this direction was very regrettable and was apt to undo a considerable proportion of the progress that had been made.

The **Authors** replied to points made in the discussion.

JUNIOR GAS ASSOCIATIONS

Eastern Junior Gas Association

"Cast Iron Pressure Pipes", *by W. D. Harrison, B.Sc.(Met.), The Staveley Iron and Chemical Company, Limited.*

Paper delivered in Cambridge on 25th January, 1961.

The author outlines the early development and describes the principal methods of producing cast iron pressure pipe to-day, namely, vertical casting, the De Lavaud and sand-spun centrifugal processes. The mechanized production of pressure pipe fittings is briefly outlined.

Requirements for pressure-tight joints and the care in handling at all stages of laying were stressed, and particular reference was made to the work done at the Iowa State College, U.S.A., on research into the magnitude of backfill loads and conditions of laying sewer pipes and culverts.

Discussion

Mr. D. G. Simpson (President) asked what developments could be expected from the sand-spun and metal-spun pipes.

The **Author** said the larger-diameter pipes were mostly sand-spun, and experience had shown that both pipes were good.

Mr. J. Anderton (Great Yarmouth) asked what pressures could be used with cast iron pipes using ordinary joints.

The **Author** said the pipe itself would stand pressure up to the bursting-point of the metal, which was 4,000 lb/sq. in, but the pressure the joint would stand was the limiting factor.

Mr. E. A. Totty (Cambridge) enquired if any experience had been gained with synthetic rubber for sealing joints.

The **Author** replied that he thought the characteristics of synthetic rubber would not be suitable for the higher pressures now being demanded.

Mr. G. W. Mason (Cambridge) asked if all fittings, tees, branches, etc., and "specials" were tested for leaks at the works.

The **Author** replied that all standard small fittings were tested with high pressure for short duration, but on the larger castings more time could be spent as a fewer number were demanded. All "specials" were subjected to test.

Mr. E. R. Fitch (Lincoln) enquired as to future trends such as the use of ductile iron.

The **Author** said he was not sure that ductile iron was going to be a commercial success; technically, it was successful, but, so far, only pilot plants were operating. There were still many snags to be dealt with before it would be perfected for general use.

"Notes on the American Gas Industry, 1960", *by A. Yates, M.I.Gas E., Technical Headquarters, Wales Gas Board.*

Paper delivered in Cambridge on 25th January, 1961.

The paper presents the Author's impression of the American gas industry, gained during a three-month tour of the United States.

Dealing with gas production and transmission, details are given of natural gas recovery, recompression, pipeline coating and laying, and flow measurement.

One section gives details of underground storage of gas, the methods of penetrating to the required depth and the injection and recovery of the gas.

A section on distribution is included, and some notes on comparative costs are given.

Discussion

Mr. D. G. Simpson (President) asked if the cost per therm in the U.S.A. was comparable with cost in this country. What pressure limits were there on pressures in pipeline bulk transmission? Was steel or cast iron favoured for low-pressure distribution systems?

The **Author** said that gas costs were comparable, but wages were higher, in the United States, and the average consumer used more gas than in this country. As regards pipeline pressures, there was no external limiting factor, but only the design and construction and materials used in the pipeline. There was no marked tendency towards the use of steel for low pressures.

Mr. W. J. Spiller (Cambridge) asked if there was any particular reason for storing liquefied petroleum gases in underground containers. Was there anything special about the gas engines used for compressors?

The **Author** said that liquefied petroleum storage vessels were partly buried below ground for reasons of safety; also, as most installations consisted of a large number of vessels, this method gave a better appearance. As regards the gas engines, these are normal, with normal ignition, *etc.*, but great care was taken to eliminate dust in order to prolong the life of the engines as long as possible. Radioactive tracers were used in the lubrication system to assess wear in some instances.

Mr. G. W. Mason (Cambridge) asked if the pipeline valves were mostly above ground, or were they protected in valve pits. Sand seemed an expensive material to use for backfilling.

The **Author** replied that most high-pressure pipelines and valves were above ground in the open country, but in towns the valves were protected in precast concrete vaults and great care was taken to exclude water. Sand was available cheaply in the instance given from Lake Michigan, which was close at hand, and this was salt-free.

Mr. H. J. Blakeley (Watford) asked if plastic pipe had been used to any extent in distribution systems.

The **Author** said that some use was made of plastic pipe, but engineers were not very happy about its use, as at some future date natural gas would give way to other gases that might soften the pipe and necessitate early renewal before the economic life of the pipe was expended.

Mr. B. J. Fuller (Watford) asked if, with the storage of liquefied petroleum gases, any steps were taken to keep the vessels cool in the high temperatures that must at times prevail in the United States.

The **Author** replied that the vessels contained propane chiefly, and a vapour pressure of 170 lb/sq. in. was the maximum pressure in hot weather. No water cooling was provided, and the fact that the tanks were partly below ground ensured that they were kept reasonably cool.

Midland Junior Gas Association

"Distribution of Gas Through Steel Pipes", *by W. Jones, A.M.I.Gas E., Divisional Distributing Engineer, North Staffordshire Division, West Midlands Gas Board*

Paper delivered at Birmingham on 24th January, 1961.

Steel pipes are in general use for the distribution of gas in the Potteries coalfield, and the Author explains the conditions encountered in a mining subsidence area and why mild steel pipes are the most suitable for use in such conditions.

Means of affording a high standard of external protection for the pipes are given with comments on factory-applied sheathing, the use of a double-moulding technique for joint protection, holiday detection, and claims made for the use of sand for bedding and backfilling the pipes.

The adequacy of internal protection with red lead is discussed: defects of this protection, arising from its initial application or from the welding of joints, are examined.

Reasons are given for the use of spigot-and-socket joints with external fillet welds, and the development is outlined of a spigot-and-socket glanded joint designed to accommodate stresses resulting from ground subsidence.

Description is given of a siphon designed to eliminate, as far as possible, the anchorage effect on a pipeline of protrusions beyond the pipe body, and to maintain the strength without interruption of the pipe body through the siphon.

A method is described for making branch connexions to live steel pipes by the welding on of wrap-around tees or branches and then under-pressure drilling the body of the live pipe.

Dust troubles in old steel pipelines are considered, and a filter having porous ceramic elements is referred to as giving the most promising solution to the extraction of dust particles from the gas stream.

The causes of leakage from steel pipes are considered, and methods for remedying these defects are described.

The connexions of services to steel pipes, including the use of a weld-on service tee, are discussed, and service-laying practices to accommodate subsidence stresses are given.

In conclusion, a plea is made for a National Research and Development Team to examine distribution methods and materials.

Discussion

Mr. R. W. Nelson (President) said he felt all would agree that Mr. Jones had presented a good paper on a subject of considerable importance today, particularly in view of the increasing use of steel for high-pressure pipelines. He remarked on how the gas industry was affected by the activities of the National Coal Board. He was interested by the section of the paper relating to the protection of pipe, and the paper itself was well-timed, but he did not agree that distribution was still the "Cinderella" of the gas industry.

Mr. B. G. H. J. Hawkings (Junior Vice-President) said that where mainlaying was concerned there was still to be found the attitude that mains laid were "out of sight and out of mind" and accountants often queried the necessity to lay pipes at all!

He had found sheathing applied at the factory to be good, but drew attention to the rapid deterioration of mild steel service tube. He thought the "Cinderella" outlook on distribution did exist. He asked whether the welds were tested

by gamma-ray or ultrasonic means, and, if so, were the tests carried out before the joints were protected by the double-moulding method.

Referring to the laying of mains in a subsidence area, Mr. Hawkings queried the use of limestone chips as part of the filling media, commenting that he would have thought that something with smaller particles would have been preferable. He also asked what method was used to mix the sand and chips.

He queried also the use of lead wool for joints, since his experience was that this material was difficult to cohere. Regarding the use of ceramic dust filters on steel pipelines, Mr. Hawkings thought that there would be some observable pressure drop, and asked how these filters were cleaned.

The **Author** said the external sheath protection of mild steel pipes was not the same as the sheathing on mild steel service tubes. With regard to the remarks leading up to the "Cinderella" reference, the point he was trying to make was that various methods used in distribution work were the results of experience, and the opinions held by the engineers concerned. What was wanted was a National Scientific Research Team to investigate all the various methods, and for them to say which was the best.

Regarding fillet welds and the testing of these welds by gamma-ray or ultrasonic means, he understood that the testing of pipeline fillet-welded joints could not readily be applied, but his own feeling was that, provided the welds passed the normal air soundness test, they were satisfactory for a medium-pressure pipeline. If there was a better method, he doubted if it could be economically justified.

The **President** interposed to say that he believed that these welds could be tested, but whether such tests could be justified would depend upon whether they were on low-pressure or on high-pressure mains.

The **Author,** continuing his reply to Mr. Hawkings, said that the limestone chips had been recommended by chemists, and were mixed with sand by using a shovel.

He confessed he was not happy about using lead wool for joints, but it should be remembered that lead-wool joints were used as being the most suitable joints then available for a mining subsidence area, and they had been reasonably satisfactory. The use of lead-wool joints was now discontinued in favour of the "Drees" glanded joint.

The use of ceramic dust filters, said the Author, was in the experimental stage, and it was hoped that cleaning might be achieved by reversal of flow through the filter. The major difficulty appeared to be the elimination of dust penetration into the ceramic filter element. Such penetration, if of any marked degree, caused difficulty in cleaning by flow reversal. It seemed that the reason for the deposition of the dust in governor installations was due to the reduction in the rate of gas flow, and the aim was, therefore, to position the filter in the gas stream before a point of reduction in flow rate.

The **President** said that this was a point of interest to the Birmingham Division of the West Midlands Gas Board, and asked if the ceramic filters were an improvement on the screen filters, and were they not dearer than the latter.

The **Author** replied that he had tried many types of filters, with no great success. The ceramic type were dearer, but, if the cost of maintenance now experienced could be eliminated, they would be worth the additional cost.

Mr. J. D. Cormack (Birmingham) said that few distributing engineers in the Birmingham Division had experienced the difficulties that faced their opposite numbers in the North Staffs. Division. Referring to the anchorage of bends in mild steel pipes used for high-pressure gas, Mr. Cormack asked how these anchorages were prepared, and were tie bars used.

As to the protection of joints with moulds, Mr. Cormack felt that there must be a tendency for the bitumen to cool as it was poured into the mould. Was it not, therefore, difficult to get it to run into the bottom of the mould?

In connexion with dust filters, he suggested that the answer with regard to governors might be to alter the design of the valve seats. Finally, he said that the breaking down of the red lead coating at weld positions was an important matter, and asked if the Author had any experience of leakage at welds due to this breakdown.

The **Author** replied that it must be remembered that the welded steel pipelines referred to were for a maximum operating pressure of only 20 lb/sq. in. At such a pressure, no anchorage was considered necessary; indeed, the reverse applied, since, in a subsidence area, it was essential that fully welded pipelines were "free floating". Stresses could then be accommodated, as had been proved in practice. Concerning the protection of joints by using moulds, the temperature of the bitumen was important, and the mould itself was usually warm, as the lime wash applied to the inner surface of the mould was hot-dried. There was no difficulty in the use of these moulds, provided these points were observed. To test the soundness of a mould, said Mr. Jones, the method used was to sound it by striking it with a hammer. Considerable force was required to break the mould, and particularly so if it were required to remove entirely the thus applied protection from the joint. Mr. Jones expressed the view that it would not be possible to alter the design of governor valves and seats to accommodate the large quantities of dust removed from the governor at the frequent maintenance visits.

As to the breaking down of the red lead coating at welds, he said that it was not yet possible to judge the long-term effect of this breakdown, since pipelines internally protected by read lead had not been long enough in service. Even so, leakage at a joint might be due to a number of reasons, and it would be difficult to relate this joint defect to destruction of the red lead coating without conducting a series of detailed tests.

Mr. Owen (Birmingham) asked how the branch connexions from live steel pipes were protected, and was the area around the valve in the pipeline also filled in with sand.

The **Author** said that the branch connexions were protected by mastic, then mastic-coated glass-woven bandage with a bitumen-backed bandage for the final wrapping; this was sufficient to ensure adequate protection. Experience had shown that the mastic affords excellent protection, the woven glass was a satisfactory carrier, and the external surface of bitumen gave protection against displacement of the mastic by abrasion resulting from movement of the buried pipeline. The method was used for all awkward contours.

He agreed there would be consolidation when using sand for backfilling on valves, but added that there was bound to be some consolidation whatever suitable material was used. The sand referred to in the paper was "medium-coarse" and in some cases grittier sand was used where drainage was required. The Author agreed that sand backfilled around the valves would not eliminate anchorage effect, and the best solution was that now adopted to install valves having cast steel bodies.

The **President** enquired if Mr. Jones had any experience of the fracture of cast iron valve bodies due to stresses at the point of anchorage; on hearing that Mr. Jones had, the President enquired if bracing was used to avoid such stresses being applied to the valve.

The **Author** replied that this was not done, since he did not feel it wise. Bracing had been considered, as had flexible couplings, but the latter had been rejected from a safety point of view. He pointed out that the difficulty would be to assess the magnitude of the movement that might be experienced, and if flexible couplings were used it would be necessary to restrict the movement of the spigot within the coupling.

Mr. J. Graham (Dudley) asked Mr. Jones if he could say what difficulties had been experienced with the use of "Torpedo" siphons, and asked if there had been any dust troubles in the siphons due to a change in the velocity of the gas. He asked also, were there any provisions for taking up the stresses in services such as the provision of lead loops.

The **Author** replied that the "Torpedo" siphon had not been in use for sufficient length of time for any difficulties that might be encountered to be experienced. He could say, however, that they had been introduced only into new pipelines, and it was not considered that dust trouble, as experienced in some of the old pipelines, would be met, due to the red

lead internal protection. Extensive dust deposits had not been experienced even with the old type of siphon in old pipelines, and it was considered that there would be little or no change of velocity in the "Torpedo" siphon. No provision for flexibility by the use of lead loops, or other such means, was considered necessary; flexibility of the service tube and the elimination of anchorage in the house structure was considered adequate, and, in general, experience substantiated this contention. In severe cases of stress, notice of the resultant movement was given by observable distortion or by a minor leakage. If provision for flexibility were made, the first sign of applied stresses causing damage to the service might be by complete collapse and, possibly, a full-bore escape. He added that in Germany the practice was to weld services and not to provide any flexible joints.

Mr. D. Dawson (Stourbridge) asked if twin sets of filters were fitted in governor inlets where dust troubles had been experienced. He referred to Mr. Jones's remarks that distribution was still regarded as the "Cinderella" of the gas industry, and asked that, if it were not possible to establish a national body to investigate and report on problems relating to the distribution of gas, could it not be done at Board level to ensure uniformity of practice at least throughout an Area.

The **Author** replied that it was necessary only to fit single filters, which would accommodate the full volume of gas passing through the governors. As to uniformity of practice at Board level, he said that divisional distributing engineers did meet to discuss problems and achieve uniformity, but different methods existed, and only impartial technical tests could determine which of the various methods was preferable.

The **President** interposed to say that distributing practice within an Area was not as diverse as Mr. Jones seemed to imply. There were in existence training schools; and he hoped, therefore, that this would lead gradually to an agreed procedure; nevertheless, there was a long way to go to achieve it.

Mr. G. Eccles (Stourbridge) asked if Mr. Jones was able to obtain information from the National Coal Board as to the pattern of mining it intended to undertake, so that appropriate action could be taken.

The **Author** said the National Coal Board did give advance information of its workings, but did not predict the surface effects of such workings.

Mr. D. T. Hall (Dudley) asked if cathodic protection were applied to steel pipes in the North Staffs. Division.

The **Author** replied that he considered that a high quality physical external protection of the pipeline was initially essential, and cathodic protection was a reinforcement of this. Cathodic protection was used, and would be applied more extensively, on major pipelines, but protecting a system of mild steel mains was a very different proposition to protecting long lengths of pipeline.

Mr. C. R. Kendall (Leicester) asked if any cold bending was done in Mr. Jones's Division, and, if so, what were the limits. He enquired also if Mr. Jones had any experience of failure of welds on seam-welded pipes of large diameter.

Mr. W. Jones said that he had no experience of cold bending, this being a practice associated with pipelining by the "spread" method, of which technique he had no personal experience. Bends used in his Division were of fabricated construction. Nor had he experience of seam-weld failure on large-diameter pipes.

Mr. A. V. Wainwright (Senior Vice-President) was interested in the protection of mild steel mains against corrosion, and said that at Shrewsbury a 1½ miles long mild steel main had been laid in sand, some 25 to 30 years ago, along a road. The main was now being replaced, and it was found that it was only badly pitted where a portion of it ran through clay, but the type of road surfacing used might have been a factor that had contributed to the corrosion.

Mr. A. V. Wainwright then proposed a vote of thanks to Mr. Jones, which was endorsed by members.

Scottish Combined Junior Gas Association

"Red Gas" *by A. E. Haffner, Ph.D., B.Sc., A.R.C.S., D.I.C., M.I.Gas E., M.I.Chem.E., F.Inst.F., Member and Chief Engineer, Southern Gas Board.*

Paper delivered in Edinburgh on 4th March, 1961.

The Author while attending a special Council meeting of the International Gas Union in Moscow in August, 1960, gained information from papers, reports, films, exhibitions and site visits about the remarkable development taking place in the Soviet gas industry.

The paper reviews the pattern of primary energy sources and the relatively high rate of expansion (32 per cent increase last year) of the use of natural gas. This is not only due to the discovery of new gasfields, but to the fuller exploitation of existing ones.

A vigorous pipelining programme is being carried out in sizes up to 42 in. and pressures up to 1,000 lb. The spread methods used are basically American, but many ingenious developments have taken place to solve Russia's own special problems set by the sometimes difficult terrain and conditions.

A pumping station on the Stavropol-Moscow pipeline was inspected. It recompresses gas in the double 28 in. (with a 42 in. being laid) mains with a recompression capacity, of 2,000 mill. cu. ft/day made up of piston and centrifugal compressors. A very small proportion of the gas pumped is Lurgi gas. Reference is made to gas-turbine compressors at the next station.

In recent years, the Russians have become accustomed to handling liquefied methane on a small, but now expanding, scale. It is not important in helping to ease the Moscow peak load, as was once intended, but is used largely as a motor fuel, particularly in refrigerated food vans or for sending in 1-ton road vehicles or 12-ton rail tankers to distant towns remote from the natural-gas pipelines.

There is a large building expansion taking place to overcome the acute housing shortage, and it is customary in these blocks of flats to supply gas unmetered, but to charge on superficial area and number of occupants. Gas cookers are regarded as fixtures and, of course, there is no competitive selling, so that appliances are simple and even thermostats are rare. The cost of gas can only be satisfactorily compared with ours by calculating the minutes to be worked by a worker to pay for a therm, and on that basis Soviet gas is less than half the price of British gas, but dearer than American gas.

The consumption of gas per head is now about the same as in this country, but is expanding annually at about 30 per cent. Much of this is industrial and some of it is interruptable, e.g., in power stations which change from gas to coal in winter. There is, therefore, not a high ratio between winter and summer, in spite of the very low winter temperatures. Underground storage has been practised for casing-head gases for some years, and a system near Moscow for town gas is about to go into use. There is active exploration (100 wells per year) in progress, and a trial, like one in Northern Illinois, is being made of storage without an anticline by providing a ring of water under pressure in a horizontal stratum.

Two ingenious schemes for maximum factory prefabrication of welded oil tanks and for coiled welded pipes inflated into a circular shape after laying, are described.

An attempt is made to compare the educational system of the U.S.S.R. and of Britain, particularly in respect of the training of engineers and craftsmen, and a conclusion is reached that engineers of comparable types are being produced at almost twice the rate per million of population as in this country.

Discussion

Mr. A. M. Jackson (Dumbarton; Vice-President, Scottish (Western) Junior Gas Association) said that he had been interested to hear of the developments in pipeline techniques and the impressive programme of work. He asked if hydraulic conveying of coal had been developed. He enquired about the scale on which underground gasification was taking place. It seemed to him that graduates were being wasted in Russia if they worked in the capacity of little more than a foreman.

Dr. A. E. Haffner replied that he had no time, in the short visit, to look at the coal industry and was unaware of any Russian development in the hydraulic conveying of coal. Their coal industry was not static, but was planned to expand by about 50 per cent in the current Seven Year Plan. Such an expansion would be a burden on the rail system, and it would not be surprising if novel forms of transport were developed.

The Russians had had about 20 years' experience, nearly all on brown coal, on much deeper deposits than the coal seams tried in England. The Russian engineers were surprised that we had abandoned our project after such a successful development stage, but thought that the thin seams, chosen by us because of coal quality and social problems, were not conducive to commercial success. By 1965, they plan to increase the output of gas from underground gasification schemes up to a level of about 200 mill. therms.

Graduates, particularly those who have had no industrial experience before going to the University or advanced engineering school, seem to be used for about a year as foremen and are then directed to their first jobs. This year helps to get the feel of labour relations just as in a graduate pupilship we try to achieve the same effect. The larger proportion of graduates in Russian industry can also be an indication of the lower standard of craftsmen's skill due to shorter apprenticeships and the larger proportion of women in industry.

Mr. R. D. Bruce (Glasgow) said he was particularly interested in new buildings, and asked what sort of gas appliances and central heating plant were being installed in the U.S.S.R.

Dr. Haffner replied that all the information he had been able to gather about appliances was shown in the text. He realized that this would not be enough to satisfy the curiosity of experts, but he was hopeful that he would eventually receive photographs and details of gas-using units following a request that he had already made. He promised to make this available to the questioner if it ever arrived. Watson House had no information on this subject.

It appeared that, as an official Soviet fuel policy, the gas industry was getting a high priority. Natural gas burnt directly for heat is better than first making electricity from it. Nevertheless, it appeared that there were district water heating schemes associated with power stations; there were also examples of electrical wall (not floor) heating.

Mr. A. G. Blackie (Paisley; President (Western) Scottish Junior Gas Association) proposed a vote of thanks referring to the fact that this was the first occasion the two junior associations had met in Edinburgh to hear the Junior Vice-President of The Institution of Gas Engineers; previously, it had been in Glasgow. This was, therefore, an important change, and the paper delivered by Dr. Haffner was well worthy of the occasion. He had presented a very wide subject in an interesting and sometimes amusing way, and all present were very grateful for this insight into the gas industry of a mysterious country.

Dr. Haffner briefly replied, saying that it was a personal pleasure to have followed in the tradition of the Junior Vice-Presidents addressing the combined Scottish Juniors. He was grateful for the interest they had displayed and appreciated their keenness in travelling long distances to attend the meeting. He wished the Juniors well in their future activities.

Scottish (Eastern) Junior Gas Association

"Cathodic-protection Installations on High-pressure Gas Pipelines in Scotland",

by W. M. R. Paterson, A.M.I.Gas E., Assistant Distributing Engineer, The Scottish Gas Board

Paper delivered in Dundee on 7th January, 1961.

In the introduction to the paper, the Author states that with the development in the gas industry, in recent years, of large-scale integration systems, and the consequent increase in working pressures, steel as a material for pipeline construction has been increasingly used, particularly in the Area of The Scottish Gas Board, where the high-pressure complete-gasification plant at Westfield delivers gas into the distribution system at a pressure of 250 lb/sq. in. For this reason, protection against corrosion has become essential. Such protection is afforded by providing (i) an adequate pipe sheathing, or (ii) cathodic protection.

The fundamental theories of corrosion and cathodic protection are briefly described and it is demonstrated that the purpose of cathodic protection is to maintain the pipeline at all times *cathodic* with respect to its surroundings by introducing an over-riding source of potential (an "impressed current") from a transformer/rectifier acting through a ground-bed.

The progress of super-grid construction within The Scottish Gas Board's Area is summarized, and the pipe coating used is described. In order to obtain information regarding the quality of the sheathing on the first section of the super-grid to be constructed, it was decided to carry out a current-drainage survey on a section of the pipeline, and this indicated that the coating was well up to standard, requiring a current density of 0·0125 mA/sq. ft. Following upon the current-drainage survey, a soil-resistivity survey was made of the entire pipeline route to determine suitable ground-bed locations.

Details of the installations provided up to December, 1960, are given, with particular reference to the first to be commissioned. Interference testing is described, and the need to notify all parties owning plant within the sphere of influence of an installation is emphasized.

Details are given regarding bonds installed, in connexion with G.P.O. cables, to combat such interference.

To ensure that the installations are operating at maximum efficiency, it is necessary to make periodic checks on the level of protection obtained. For this purpose, test-points have been selected, along the pipeline route, where regular potential measurements are taken. Record cards are illustrated, which indicate readings at a typical test-point and at a rectifier installation; these show that the installation is working satisfactorily at two-thirds of its maximum rated capacity, giving full protection to approximately 21 miles of 12¾ in. outside-diameter pipeline at a current density of 0·018 mA/sq. ft.

Discussion

In the discussion that followed, the question of corrosion by stray currents was raised, and the **Author** suggested that the only satisfactory way of dealing with such corrosion was to locate the source of the stray current, and eliminate it, by suitable bonding, if necessary.

The powers of the Joint Committee for the Co-ordination of Cathodic Protection were discussed, and it was pointed out that, while this Committee's recommendations were not mandatory, any interference that caused damage to another undertaking's plant would be the legal liability of the authority responsible. It was thus to the mutual advantage of all concerned that the Committee's recommendations should be accepted.

Further points raised included the training of personnel for routine supervision of installations, the efficient wrapping of welded joints, and the anticipated life of steel pipes receiving cathodic protection.

"The Accountant's Place in The Scottish Gas Board", *by A. MacPherson, C.A.*

Paper delivered in Kirkcaldy on 4th February, 1961.

The Accountant must be the book-keeper and financial adviser to the Board in all aspects of its financial relationships within itself and with its customers and his department must, therefore, be organized to give a comprehensive service to the management of the Board in its widest sense, to their customers and to the Board's employees as individuals.

The Chief Financial Officer is concerned with the administration of the Finance Department and with the financial policies at the level of the Board in all questions of major policy, and administers, on its behalf, its finances, including the administration of the superannuation funds. In addition, he is responsible for rating and valuation, taxation, statistics and audit.

The Divisional Accountant and his staff are more essentially the book-keepers of the Board. A very large part of their activities is devoted to the running of the Board's accounting, its meter reading, its debt collection, its ledgers and its financial statements. These are the activities of the Accountant and are necessary in order that the funds of the Board may continue to flow smoothly.

The Accountant at divisional level, however, must do more than these routine tasks and must provide a service to management. This service can be done by statistics, financial statements and costing and budgetary methods. Costing and budgetary control are very valuable tools of management, and management personnel at all levels must not be put off by a feeling that this is something beyond them and which they do not understand. Budgeting is no more than deciding how far one can go with a given sum of money, whether it be a weekly pay packet or a Board's production programme; and costing, a division of the sums spent into individual items or processes and an examination of the component parts of these costs. It is little more than the prudent housewife does in planning her housekeeping, and good costing and budgetary control means good housekeeping in its widest sense.

The Accountant must always remember that the information produced must be concise and of use to those members of management who are intended to use it. There is little profit in the production of reams of paper that no-one has the time or the effort to read in any detail. The information supplied must be concise, timely and in readily readable form in order that management may quickly appreciate trends and movements and take the appropriate action.

The Accountant must also maintain staff records on behalf of all employees and look after, on their behalf, their remuneration and deductions therefrom in respect of superannuation and income tax, and, indeed, he could probably claim that his is the only Service Department of the Board that remains interested in an employee after he has retired.

The Accountant must be an essential part of the management team and must maintain the services necessary from his department for the guidance of management and of the Board in their relations with their employees and the public.

Discussion

Mr. J. T. Christie (Aberdeen), having considered cost and other statements designed to examine the efficiency of production methods, asked if any statements could be produced to demonstrate the efficiency or otherwise of the accounting function.

The **Author** said costs were produced per customer and per account rendered, which could show the same trends as were produced in manufacturing cost statements.

Mr. J. T. Pay (Dundee) suggested that the Accountant tended to look at nothing beyond the financial figures, and this could have serious effects on customer service when the costs of maintaining adequate stocks were regarded as being additional interest charges.

The **Author** said there must be reason in all things, and no Accountant could take any exception to stocks, in reasonable quantities, but every one knew instances where stocks were held for unreasonable periods, and, in addition to interest charges, Boards could be involved in losses through depreciation and deterioration.

Mr. Affleck (Perth) asked what is the opinion of the Accountant relating to the forceful type of salesman employed by commercial concerns and the Boards, having regard to the possible eventual hire purchase bad debt.

The **Author** said that in his opinion the emergence of bad debts following the employment of this type of salesman must necessarily be a calculated commercial risk taken in the best interests of the Board.

Mr. D. C. Elgin (Edinburgh) said firstly that what the gas industry mostly required of every one of its employees at the present time is the maximum benefit of their mature experience, both individually and within the teams that still, in effect, comprise the management group at all levels. Thus the labels marked "Accountant" or "Engineer" or "Salesman", with which they were classified should not delude them into forgetting their common aim. A good Accountant was first of all a man of mature experience and sound judgment, who, by virtue of his present qualities, had a contribution to make to the sound running of the industry; the fact that he looked at things from the financial point of view was almost secondary. All this was particularly true at the highest levels of management, and applied equally to the Engineer. For this reason alone, the Juniors must welcome Mr. MacPherson's excellent paper.

Secondly, he said that one important field in which the close participation of the Accountant and Engineer was required was in the preparation of the forward estimates, which determined the effectiveness with which quite large sums of money, and certainly all that was available to them, were employed. This was an exceptionally difficult process to get right; should aggregate estimates be built up from district or divisional forecasts, or should a central plan be drawn up and allocations assigned to the other levels? Some compromise might be necessary, but the aim must be to provide, on the smallest budget possible, that combination of assets that would best serve the Board for the longest period. One factor that always arose in taking decisions on the provision of new plant and the pensioning-off of old, was the depreciation rate, and he would like to see some alterations. A depreciation rate based on some arbitrary expectation of life was quite unsatisfactory and did not take into account any changes for the better or the worse that were found to be true after a plant was commissioned. For example, an improvement in the performance of a plant was seldom taken into account in the rate of write-off, and a true comparison could not be made with replacement alternatives.

Thirdly, under the final two columns of the cumulative Opening Statement an "improved variance" of £6,327 was shown under the heading "Other Factors". This was a large proportion of the total variance, and he suggested that if the statement was to play a full part in operational control this omnibus heading should be kept for relatively small items, and as few of these as possible. This might mean an increase in the number of specific variance headings.

His final point emerged from the earlier comments on billing. He felt strongly that in routine transactions with the public they should take the opportunity to present an image of brisk efficiency and should not thereafter burden existing customers with wordy instructions, unnecessarily lengthy addresses, or irksome details such as instructions to add "and Co." or "A/c. Payee" to crossed cheques; these were quite useless embellishments.

The **Author** replied that the rates of depreciation used by the Board were based on standard rates for the gas industry. It would be agreed that these rates took into account the usage of the plant, and very many good arguments could be brought up for a rate based on the usage of the plant, which would, therefore, enable it to be written off within its useful life. Unfortunately, a certain amount of semi-statutory information required to be incorporated in the account, which was not always necessary in the case of commercial concerns, and every endeavour was made all times to keep this information down to a minimum.

Western Junior Gas Association

"Some Aspects of Automatic Control on Holder Stations", *by D. D. Way, A.M.I.Gas E.*

Paper delivered at Exeter on 18th February, 1961.

The paper details some of the important factors determining the operation of automatic equipment associated with a gas-holder station.

The Influence of Load Factor on the Economics of Gas Distribution

In order to transfer a quantity of gas between two points in a given time at minimum cost, the delivery should be at constant rate. Whether this can be attained in practice depends on the ratio of the number of consumers fed from holder stations to those fed directly from the high-pressure main, and also upon the holder stock available. An expression is derived showing the minimum value of this ratio below which it is not possible to obtain a load factor of unity:

$$\frac{\text{Number fed from holder stations}}{\text{Number fed from H.P. main}} = 24\,\frac{Qm}{Qd} - 1$$

where Qm = maximum hourly consumption per consumer,

Qd = average daily consumption per consumer.

High terminal pressures are often caused by a poor load factor and have a very bad effect on the costs of gas compression, principally where there is no control over demand. A method using partial remote control is considered with a view to achieving part of the savings possible with full remote control.

The Volumetric Governor

Consideration is given to the important part played by the volumetric governor both in making maximum use of the holder stocks available and improving the load factor of the high-pressure distribution system. Seven basic functions of this governor are set out, and particular regard is given to the importance of safety both in protecting high- and low-pressure supplies.

Automatic Boosting

The common method of using time and pressure switches wired in parallel can lead to a certain amount of unnecessary boosting, especially on stations where the holder-main and district pressures vary appreciably. A suggested method of control is outlined, using the differential between holder and district pressures.

Safety Governors

The size of a safety governor should be related to the carrying capacity of the high-pressure main. The governor may be arranged to operate at normal town pressures, once in action. An effective method described was devised by Mr. A. G. Holtam (Cheltenham).

Station Governor

Two of the basic functions of a station governor are: (i) taking the town as a whole, the fluctuation in pressure should be a minimum; (ii) the average pressure should be the lowest possible to maintain a satisfactory supply over the whole district.

The methods of step pressure and gradual increases, using an auto-pilot governor, are compared with the above conditions in mind.

Anti-freeze Protection on Gasholders

On a holder station requiring only periodic attention, consideration should be given to methods of automatic protection against the freezing of holder water. The method chosen will be mainly governed by the capital and running costs. Estimated capital costs for one particular holder were:—Electric, £1,500; gas-fired steam boiler, £950; gas-fired hot water circulation, £500.

The differences in running cost appear to be small when comparing gas with electricity, so long as maximum demand charges do not have to be paid. Consideration is given to various methods of heating the cups and tanks of holders, with particular reference to ways of admitting and returning water on a gas-fired hot water circulation system.

Discussion

Mr. D. H. P. Hammond (Weston-super-Mare) commented that it would have been possible to write a complete paper on almost any one of the items Mr. Way had included; he had indeed undertaken an astronomical task. He asked if Mr. Way had undertaken any research to establish the minimum effective storage capacity necessary to permit a 24 hr constant-rate intake to the station. In his experience, 8 hr storage capacity based on peak winter day output was about right for a normal district without any large industrial loads.

He was surprised that Mr. Way had not mentioned the storage capacity of the high-pressure system itself, since this could be very effective in spreading out some of the load variations by the "line packing" technique.

He endorsed the use of overspill governors as a means of securing a better load factor, and commented that he was pleased to see the sensible approach adopted towards safety governors.

He had been very interested in the section on holder anti-freezing, and commented on the relation between capital costs and running costs, pointing out that relatively high running costs over a very short period might prove relatively cheaper than a high initial capital cost. He favoured the use of more gas-fired installations and mentioned the installation now in operation at Launceston holder station as being typical of what could be done. He suggested that careful consideration was necessary before undertaking drilling of cups to form internal overflows, since there was a danger of the cup blowing.

The **Author** stated that he had not undertaken any tests to establish the minimum effective storage required, but he agreed that 33⅓ per cent of peak winter day was about right.

With regard to the use of "line packing", he pointed out that the economics required examination in each case before deciding to adopt this policy.

Mr. Annakin (Plymouth) said that, as the Distribution Engineer responsible for Launceston, he was very pleased with the operation of the holder anti-freeze installation. In fact, due to the mild winter, it had been possible to keep the holder completely clear, merely by circulating water through the system by means of the pump with no heating, whereas an electrical system would have been in operation and consuming current.

He wondered if Mr. Way had any experience of holder control gear freezing, and asked if there was any means of preventing this. On the question of automatic booster operation, he asked if Mr. Way's proposed system would prevent the booster starting, say, at night, when lower pressures were required on the district.

They had practised "line packing" in Cornwall for some time, but he felt that economically it was better to operate the system at the minimum possible pressure at any one time, but there might be an operational justification for "line packing" depending on local conditions.

The **Author,** replying to Mr. Annakin's question on holder operating gear, said that he had no direct experience of freezing taking place, but added that he thought Mr. Green (Bryan Donkin Company Limited), who was present, might be able to comment on this.

With regard to his proposed method of controlling boosting, he pointed out that as long as there was an adequate differential across the booster and governor the booster would remain out of action, and it was only when the differential fell below the pre-set figure that the booster would operate.

Mr. Green (Bryan Donkin Company, Limited) confirmed that it was possible, under extreme weather conditions, for freezing of the holder control gear to occur, and mentioned that his firm had in fact designed a small thermostatically controlled heater unit for use in exposed situations.

Mr. Manning (Bristol) asked if the Author had any running costs available for anti-freezing on, say, 50,000 and 750,000 cu. ft gasholders.

The **Author** gave some calculated figures for electrical anti-freezing, but pointed out that these were based on a unit charge and did not take account of maximum demand charges.

Mr. J. B. Taylor (Bath) spoke of the possibility of a diesel-engined compressor pulling up, due to lack of variable torque characteristics, when intake to holder stations was suddenly curtailed.

The **Author** agreed there was a possibility in theory of this happening, but suggested that staggering of intake schedules should be arranged to avoid such extreme variations in loading.

Mr. Hammond said that with a large integration system there was a considerable time lag on the system, and any appreciable fall-off in the load would be met by either unloading one cylinder of the compressor or changing over to a smaller compressor.

Mr. Ross (Bristol) referred to the previous discussion regarding the relative merits of the various holder anti-freezing systems. He pointed out that it should be possible to obtain electricity at night on off-peak tariff and wondered if this would not be cheap enough to justify the installation of an electrical system.

The **Author** replied that even at off-peak prices there was a reduction cost by using gas as the fuel rather than electricity.

The **President** referred to the comments of Mr. Hammond and Mr. Annakin on "line packing", and said that in his view there might be cases where judicious use of "line packing" on a selected system might effect a saving in costs.

Mr. C. R. Winter (Bath) proposed a vote of thanks to Mr. Way for a clear, concise paper of extremely high quality. He was grateful to Mr. Way for undertaking the preparation of his paper, and it was obvious that he had a real interest in the subject.

Library Accessions

The following are a few additions to the Library since the issue of the *Journal*, Vol. 1, No. 3, March, 1961:

Britain's Scientific and Technological Manpower, by G. L. Payne. Oxford, 1960.

British Ceramic Research Association:

Flaking in Continuous Vertical Retorts: A Study of Photogrammetric and Mechanical Methods of Measuring the Depth of Flaking at Working Temperatures, by J. F. Clements and L. Sabiston. *Research Paper* 478, 1960.

A Note on the Significance of "Critical Strain" in the Flaking Problem, by N. F. Astbury, W. R. Davis and F. T. M. Smith. *Research Paper*, 477, 1960.

Refractories in Oil-gas Plants, Part 2: Further Observations on Their Behaviour, by L. Sabiston. *Research Paper* 479, 1960.

British Standard 1016: Part 10: 1960 (Methods for the Analysis and Testing of Coal and Coke. Part 10: Arsenic in Coal and Coke).

British Standard 1251: Part 4: 1960 (Specification for Open Fireplace Components. Part 4: Lintels).

British Standard 1344: Part A1: 1960 (Specification for Vitreous Enamel Finishes. Group A. Kitchen Equipment. Part A1: Resistance to Thermal Shock).

British Standard 1344: Part A2: 1960 (Specification for Vitreous Enamel Finishes. Group A. Kitchen Equipment. Part A2: Resistance to Culinary Acids).

British Standard 1523: Section 2: 1960 (Glossary of Terms Used in Automatic Controlling and Regulating Systems. Section 2: Process Control).

British Standard 3316: 1960 (Specification for Large Incinerators for the Destruction of Hospital Waste).

British Standard 3323:1960 (Glossary of Coal Terms).

British Standard 3328: 1961 (Specification for Domestic Gas Pokers and Portable Underbar Ignition Burners).

Chemical Engineering Practice, edited by H. W. Cremer and S. B. Watkins. Vol. 10: Ancillary Services. (Butterworths, 1960.)

Clean Air Conference, Harrogate, 1960: Papers Presented. (National Society for Clean Air.)

Flammable Gases. Fire Protection Association *Technical Information Sheet* 3015.

Mechanical Properties of Structural Materials at Low Temperatures. A Compilation from the Literature, by R. Michael McClintock and Hugh P. Gibbons. *U.S. Department of Commerce, National Bureau of Standards, Monograph* 13, 1960.

Natural Gas, by R. L. Borden. *Department of Mines and Technical Surveys, Ottawa, Review* 56, 1959.

Proceedings of the Symposium on Recent Mechanical Engineering Developments in Automatic Control, London, January, 1960. (The Institution of Mechanical Engineers.)

Safety in Air and Ammonia Plants. American Institute of Chemical Engineers.

Soviet Education for Science and Technology, by Alexander G. Korol. (John Willey; 1958.)

Ultrasonic Welding. (American Welding Society, 1960.)

U.S. Bureau of Mines:

The Fischer-Tropsch Synthesis Using Gas Recycle Cooling (Simulated Hot-gas-recycle Process), by D. Bienstock and Others. *Report of Investigations* 5655, 1960.

Hydrogenating Coal in a Pilot Plant with a Molybdenum Catalyst, by H. H. Ginsberg and Others. *Report of Investigations* 5673, 1960.

Producing Heavy Fuel Oil by Hydrogenating Bituminous Coal, by H. H. Ginsberg and Others. *Report of Investigations* 5674, 1960.

Underground Gasification of Coal. Hydraulic Fracturing as Method of Preparing a Coal Bed, by J. P. Capp, and Others. *Report of Investigations* 5666, 1960.

World Solid Fuels, Electricity, Gas, Iron and Steel, and Petroleum Statistics. (Ministry of Power, 1961.)

Year Book of the Heating and Ventilating Industry, 1960-61.

Forthcoming Meetings

The following meetings have been arranged for the six weeks commencing 1st April, 1961:

(*a*) District Sections and an Affiliated Association

THE INSTITUTION OF GAS ENGINEERS—EASTERN SECTION

26th April	Morning Visit to Eastern Gas Board, Gas Works, Newmarket Road, Cambridge. (10.30 a.m. to 12.30 p.m.) Luncheon by invitation of the Eastern Gas Board. (12.45 p.m. The Dorothy Restaurant, Sidney Street, Cambridge.) General Meeting. Paper, "Some Aspects of the Accounting Function in the Gas Industry", by H. R. Hazeldine. (2.45 p.m. The Dorothy Restaurant, Sidney Street, Cambridge.)

THE INSTITUTION OF GAS ENGINEERS—LONDON AND SOUTHERN SECTION

18th April	Paper, "The Reduction of the Carbon Monoxide Content of Town Gas", by K. W. Francombe. (2.45 p.m. The Caxton Hall, Caxton Street, London, S.W.1.)
9th May	Annual Luncheon and Chairman's Address. (The Connaught Rooms, Great Queen Street, London, W.C.2.)

THE INSTITUTION OF GAS ENGINEERS—MANCHESTER AND DISTRICT SECTION

21st April	Annual General Meeting. (Queen's Hotel, Manchester.)

THE INSTITUTION OF GAS ENGINEERS—MIDLAND SECTION

14th April	Annual General Meeting. Luncheon. (12.15 p.m. for 12.45 p.m. Penns Hall Hotel, Walmley, Sutton Coldfield.)

THE INSTITUTION OF GAS ENGINEERS—NORTH OF ENGLAND SECTION

27th April	Joint Meeting with the Northern Section of The Coke Oven Managers' Association. Paper, "The Production, Treatment and Disposal of Effluent Liquors", by E. T. Pickering. (7 p.m. Three Tuns Hotel, Durham City.)
4th May	Annual General Meeting and Ladies' Day. (Hexham, Northumberland.)

THE INSTITUTION OF GAS ENGINEERS—SOUTH WESTERN SECTION

10th May	Morning Visit to the Exeter Manufacturing Station and the Appleby-Frodingham Plant. (11 a.m.) Luncheon. (1 p.m. Rougemont Hotel.) Paper on the Appleby-Frodingham Plant, by L. Baldwin. Film of the Sharpness bridge incident. Paper, "The Underwater Crossing of the River Severn", by R. Pratt. (2.15 p.m.) Tea (4.30 p.m.)

THE INSTITUTION OF GAS ENGINEERS—WALES AND MONMOUTHSHIRE SECTION

28th April	Spring Meeting. (Tenby.)

IRISH GAS ASSOCIATION

3rd and 4th May	Annual General Meeting

(*b*) Junior Gas Associations

EASTERN

19th April	Visit to Stewarts and Lloyds, Limited, Corby, Northamptonshire.
27th April	Visit to Stewarts and Lloyds, Limited, Corby, Northamptonshire.

LONDON AND SOUTHERN

7th April	Paper, "Laboratory and Field Experience in Warm-air Heating", by E. W. G. Dance and P. R. Chance. (6.30 p.m. Westminster Technical College, Vincent Square, London, S.W.1.)
27th April	Visit to Robert Cort and Son, Limited, Reading.
28th April	Paper, "Big Inch Steel High-pressure Pipelining Against Odds", by J. E. Gray and J. W. Yates. (6.30 p.m. Westminster Technical College, Vincent Square, London, S.W.1.)
12th May	Annual General Meeting. (6.30 p.m. Westminster Technical College, Vincent Square, London, S.W.1.)

MANCHESTER

8th April	Visit to the Partington Works of the North Western Gas Board. Paper, "Development in the Utilization of Refinery Gas at Partington", by N. Hoyle.
26th April	Visit to the Derbyshire Silica Firebrick Company, Limited, Friden, Derbyshire.
9th May	Joint Meeting with the Yorkshire Junior Gas Association. Visit to the Works of Newton Chambers and Company, Limited, Thorncliffe, Near Sheffield.

MIDLAND

18th April	Annual General Meeting. Paper, "Development in the City of Birmingham", by B. R. Cowles. (Staff Mess Room, West Midlands Gas Board, Council House, Birmingham.)
12th May	President's Day.

NORTHERN

28th April	Special-speaker Meeting. Paper, "Training in Distribution", by W. H. B. Porter. (2.30 p.m. Gas Showrooms, Newcastle-upon-Tyne.)
13th May	Visit to Stockton District, Northern Gas Board. Paper, "Gas Governing", by R. Hutchinson, (2.30 p.m.)

SCOTTISH (EASTERN)

8th April	Paper, " Pipeline under the Forth ", by R. O. Emmony. (Dunfermline.)
13th May	Annual General Meeting and Outing. (Edinburgh.)

SCOTTISH (WESTERN)

7th April	Paper, " Pipeline under the Forth ", by R. O. Emmony. (6.30 p.m. Industrial Section, 9, George Square, Glasgow.)
28th April	Annual General Meeting. Paper, " Education and Training ", by A. S. C. Morton. (St. Enoch's Hotel, Glasgow.)

WESTERN

12th April	Visit to the Works of W. D. and H. O. Wills, Limited, Bristol. (2 p.m. East Street, Bedminster.)
13th May	Visit to the Hollacombe Works of the South Western Gas Board, followed by an Open Forum.

WALES AND MONMOUTHSHIRE (NORTH AND SOUTH)

27th April	Annual General Meeting. (Llandrindod Wells.)

YORKSHIRE

5th April	Visit to William Asquith, Limited, Halifax.
26th April	President's Day. Visit to W. C. Holmes and Company, Limited.
9th May	Joint Meeting with the Manchester Junior Gas Association. Visit to the Works of Newton Chambers and Company, Limited, Thorncliffe, Near Sheffield.

(*c*) Kindred Bodies

Members of The Institution of Gas Engineers who wish to attend any of these meetings, but are not members of the bodies concerned, should apply to the appropriate Secretary at the address indicated.

THE INSTITUTE OF FUEL

(18, Devonshire Street, Portland Place, London, W.1.)

18th April	Melchett Lecture. " Radiative Transfer in Combustion Systems ", by Professor H. C. Hottel. (5.30 p.m. Royal United Service Institution, Whitehall, London, S.W.1.)
19th April	Paper, " Ceramics and Brick Kilns ", by J. Fleming. (8 p.m. Dublin.)
20th April	Annual General Meeting. Paper, " Recent Developments in the Production of Town Gas ", by G. Milner. (6.30 p.m. Gas Showrooms Lecture Theatre, Nottingham.)

THE INSTITUTE OF PETROLEUM

(61, New Cavendish Street, London, W.1.)

3rd May	Paper, " New Ideas in Welding for the Petroleum Industry ", by W. K. B. Marshall and V. I. Holmes. (The Lecture Theatre, The Institute of Petroleum, 61, New Cavendish Street, London, W.1.)

THE INSTITUTION OF CHEMICAL ENGINEERS

(16, Belgrave Square, London, S.W.1.)

11th April	Joint Meeting with the Chemical Engineering Group. Paper, " A Systematic Classification of Chemical Processes and Equipment ", by K. Fischbeck. (6 p.m. The Society of Chemical Industry, 14, Belgrave Square, London, S.W.1.)
18th April	Joint Meeting with The Institute of Petroleum. " Recent Developments in the Production of Olefines and Aromatics by Petroleum Cracking ", by M. Ruhemann D. R. Cummings and W. L. Seddon. (North Western Branch, Manchester.)
19th April	Paper, " Some Corrosion Problems in the Chemical Industry", by D. Bennion. (7.30 p.m. North Western Branch Grosvenor Museum, Chester.)

THE INSTITUTION OF STRUCTURAL ENGINEERS

(11, Upper Belgrave Street, London, S.W.1.)

7th April	Annual General Meeting. Paper, " Mechanical and Electrical Problems Associated with Multi-storey Construction", by G. K. Medlock, followed by a film on " The Pirelli Building in Milan ". (6 p.m. Small Lecture Theatre, University Engineering Laboratories, University Walk, Bristol.)
28th April	Annual General Meeting. Paper, " Modern Urban Highway Structures", by G. B. Smedley and G. M. Mills. (6 p.m. The Byng Kenrick Suite, College of Advanced Technology, Gosta Green, Birmingham, 6.)

THE ROYAL INSTITUTE OF CHEMISTRY

(30, Russell Square, London, W.C.1.)

6th April	Joint Meeting with the South-East London Section of The Institute of Petroleum. Paper, " Isotopes in Industry ", by W. G. Busbridge. (7 p.m. The Sun Hotel, Chatham.)

THE INSTITUTION OF PLANT ENGINEERS

(2, Grosvenor Gardens, London, S.W.1.)

5th April	Paper, " Radioactive Isotopes in Industry ". (7.30 p.m. The Grand Hotel, Bournemouth.)
24th April	Paper, " The Introduction of Planned Maintenance Systems ", by A. F. Stedman. (7.30 p.m. The Houldsworth School of Applied Science, The University, Leeds, 2.)
25th April	Paper, " Fuel Efficiency ", by W. Short. (7.30 p.m. The South Wales Engineers' Institute, Park Place, Cardiff.)

Personal Notes

Appointments

(a) By Area Gas Boards :

SCOTTISH GAS BOARD

Grid Engineer : **J. W. G. Sutcliffe**
Deputy Grid Engineer : **A. O. Llewellyn**
Assistant Distributing Engineer : **W. M. R. Paterson**
Dumbarton Works—
Technical Assistant : **F. H. Joynes**

WEST MIDLANDS GAS BOARD

Wolverhampton District—
District Manager : **W. Williams**
Tipton District—
Station Engineer : **F. Wardle**

EAST MIDLANDS GAS BOARD

Aylestone Works—
Assistant Engineer : **J. R. Lane**

(b) Other Appointments :

Mr. J. H. Roditi (A) has recently taken up an appointment as Specialist Engineer (Pipelines) with the Kellogg International Corporation, London.

Mr. W. Morland Fox (M) has been appointed President of the Mechanical Handling Engineers' Association.

Mr. W. A. P. Hoskin (M) Technical Director of The Barnsley District Coking Company, Limited, has been appointed to the Board of the parent company, Barrow Barnsley (Holdings), Limited.

Addresses Required

The Council would be grateful to receive the present addresses of the following members, last heard of in the places given in brackets :—

Mr. E. Clark (Bridlington).
Mr. O. Clyne (Huddersfield).
Mr. M. J. Green (London).
Mr. S. W. Hayes (Braunton).
Mr. E. F. Surti (India).
Lt.-Col. T. C. Whimster (Ashford).

General Notices

Overseas Gas Associations

The Annual General Meetings of the following overseas Gas Associations will be held during 1961, on the dates and at the places indicated: —

(*a*) American Gas Association, on 1st to 4th October, at Dallas, Texas.
(*b*) Austrian Gas Association, on 16th to 19th May, at Baden, near Vienna.
(*c*) Belgian Gas Association, on 7th and 8th June, in Brussels.
(*d*) Canadian Gas Association, on 20th to 24th June, at Banff, Alberta.
(*e*) Danish Gas Association, on 16th to 18th May, at Alborg.
(*f*) French Gas Association, on 14th to 17th June, at St. Malo.
(*g*) German Gas Association, on 29th to 31st May, in Berlin.
(*h*) Japan Gas Association, on 18th May, in Tokyo.
(*i*) Netherlands Gas Association, on 10th to 12th July, at Eindhoven.
(*j*) Swedish Gas Association, on 27th to 30th June, in Stockholm.
(*k*) Swiss Gas Association, on 8th to 10th September, at Brunnen.

The Secretary of the Institution would be glad to hear of any member who plans to be present at any of these overseas meetings.

Royal Society of Arts

The Royal Society of Arts offers the following prizes during 1961: —

(*a*) Howard Prize (£50) to the author of a treatise on some aspect of the subject of motive agents.
(*b*) Fothergill Prize (£20) for a descriptive essay, or model, embodying some new idea for the prevention or suppression of fire.

Entries must be received, not later than 31st July, 1961, by the Secretary, Royal Society of Arts, 6 to 8, John Adam Street, London, W.C.2, from whom further particulars may be obtained.

The Institution of Plant Engineers

The 14th Annual Conference of The Institution of Plant Engineers will be held in Blackpool on 19th to 21st April, 1961. The Conference will be open to a limited number of non-members from industrial concerns who wish to nominate senior staff to attend.

The programme will include papers on complex automation and on causes and prevention of corrosion; also discussions on the provision of specialist information, broadening the engineer's outlook, simplification of maintenance planning methods, and utilization and development of engineering methods of lifting.

Further particulars may be obtained from the Secretary, The Institution of Plant Engineers, 2, Grosvenor Gardens, London, S.W.1.

The Pipeline Industries Guild

An all-day Symposium, entitled "Economics of Pipelines," will be held by The Pipeline Industries Guild on Tuesday, 11th April, 1961, at Caxton Hall, Westminster. Three papers, by personalities in the gas, oil and water industries, will be introduced.

The meeting is open to all persons interested in the subject, and applications for tickets and the pre-printed papers should be made to the General Secretary, 7, Iddlesleigh House, Caxton Street, London, S.W.1. The inclusive fee will be £1 1*s*.

Engineering, Marine, Welding and Nuclear Energy Exhibition

This Exhibition will be held at Olympia, London, on 20th April to 4th May, 1961.

A complimentary ticket of admission is enclosed with this issue of the *Journal*.

Conference on the Problem of Communication

This Conference, organized by the Department of Scientific and Industrial Research, will be held in the Brangwyn Hall, Swansea, on 18th and 19th April, 1961. Speakers will describe present-day methods of obtaining and disseminating information, examine their limitations, and suggest improvements. A large proportion of the time will be available for discussion. The Conference is particularly aimed at industrial management and research management, and at all those concerned with the adoption of new ideas.

Further details and a form of registration may be obtained from the Conference Secretary, D.S.I.R. Office for Wales, Block 2, Government Buildings, Gabalfa, Cardiff.

Refrigeration and Air Conditioning Exhibition and Convention

The Second International Refrigeration and Air Conditioning Exhibition will be held at Earls Court, London, on 11th to 14th April, 1961. It will include machinery and equipment for every kind of refrigeration, air conditioning and mechanical cooling.

During the Exhibition, there will be a Convention at which a number of papers will be presented.

Further particulars, registration form and complimentary ticket of admission to the Exhibition may be obtained from the Secretary of The Institution of Gas Engineers.

Industrial Finishes Exhibition and Convention

The First International Industrial Finishes Exhibition will be held at Earls Court, London, on 8th to 11th May, 1961. It will incorporate metal pre-treatments, paints, electro-plating, galvanizing, metal colouring, anodizing, plastic covering, vitreous enamelling, shot-blasting, vacuum deposition, instrumentation, and all ancillary equipment for the finishes of industrial products.

A complimentary ticket of admission may be obtained from the Secretary of The Institution of Gas Engineers, and further particulars from Scientific Surveys, Limited (Exhibition Division), 97, Old Brompton Road, London, S.W.7.

Building Trades Exhibition

The Second Northern Building Trades Exhibition will be held in the New Exhibition Hall, Harrogate, on 15th to 22nd April, 1961.

A complimentary ticket of admission may be obtained from the Secretary of The Institution of Gas Engineers.

Society of British Gas Industries Golfing Circle

The Circle will hold a Meeting on Monday, 15th May, 1961, at the Royal Mid-Surrey Golf Club, Old Deer Park, Richmond, Surrey. The competition for the Coronation Plate, played for annually by members of The Institution of Gas Engineers who are, on the day of the competition, full-time members or officials of The Gas Council and/or a Gas Board, will take place at this meeting.

Intending competitors should apply for full particulars and entry forms to the Honorary Secretary of the Circle (Mr. C. T. C. Woodall, M.B.E.), 255, North Circular Road, Neasden, London, N.W.10.

Library

The Library and Reading Room of the Institution are open on weekdays between 9 a.m. and 5.30 p.m. Members may borrow books by post, excepting books of reference and certain others, on application to the Secretary.

Benevolent Fund

Contributions to the Benevolent Fund of the Institution may be paid at any time to the Honorary Secretary of the Benevolent Fund, 17, Grosvenor Crescent, London, S.W.1. It is a convenience if annual contributions are made by banker's order, and it is particularly advantageous to the Fund if such contributions are made by Deed of Covenant, whereby the Fund is able to reclaim from the Inland Revenue an appropriate sum in respect of income tax paid by the contributor. Further particulars, with deed forms and banker's orders for completion, are obtainable from the Honorary Secretary of the Fund.